Crystal-field and Nd-Mn Exchange Interaction in Nd$_{2/3}$Ca$_{1/3}$MnO$_3$

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**Abstract.** A study of the low field magnetization and specific heat in magnetic fields up to 9 T of Nd$_{2/3}$Ca$_{1/3}$MnO$_3$ perovskite in the 2-30 K temperature range has been done. All the specific heat data show broadened Schottky-like anomaly below 20 K. We suppose that such a behavior originates from the Nd magnetic ordering caused by the splitting of the Nd$^{3+}$ ions ground-state doublet (GSD) in the effective molecular field $H\text{_{eff}}$ of Mn spin system supplemented by an applied external magnetic field. The zero field GSD splitting is an evidence of a strong exchange coupling between Nd and Mn magnetic subsystems. The Nd-ions magnetic ordering introduces an additional contribution to the ferromagnetic moment producing anomalies of the field-cooled and zero-field-cooled magnetizations of the system below 28 K. The broadened Schottky-like anomalies found are fitted for every field by a set of three Schottky functions. Applied magnetic field extends the anomaly region and shifts it to the higher temperatures. Splitting of the higher crystal field Kramers doublets gives an additional contribution to the heat capacity under magnetic fields. The GSD g-factors $g_\parallel$ and $g_\perp$ was estimated as 3.4 and 2.2, respectively, and $H\text{_{eff}}$ as 9 T.

1. Introduction

One of the most intriguing fundamental problem in the physics of perovskite manganites R$_{1-x}$A$_x$MnO$_3$ (R – rare earth, A – divalent alkali earth metal) is an interaction between different spin systems. Recently it was shown that a strong interaction between Nd and Mn spin systems does exist in Nd$_{2/3}$Ca$_{1/3}$MnO$_3$ perovskite [1]. According to the neutron diffraction study the room temperature crystal structure of Nd$_{2/3}$Ca$_{1/3}$MnO$_3$ corresponds to the standard orthorhombic $Pnma$ space symmetry. Below charge ordering at $T_{CO} \approx 212$ K its behaviour is consistent with a self-organized phase separated scenario [2, 3]. It experiences two antiferromagnetic (AF) transformations at about 130 K and 80 K and a ferromagnetic one at about 70 K, so one can expect a coexistence of at least three different long range magnetic orderings at low temperatures: the antiferromagnetic of DE and pseudo-CE type ones, and the ferromagnetic of B-type one (classification is in accordance with [4]).

Temperature dependent heat capacity $C(T)$ of Nd$_{2/3}$Ca$_{1/3}$MnO$_3$ has shown a broad Schottky-like anomaly below 20 K, attributed to the splitting of the ground state doublet (GSD) of Nd$^{3+}$ ions caused by the ferromagnetic component of AF structure of Mn spins [1]. The anomaly found was considered...
as an evidence of a strong Mn-Nd exchange interaction. The experimental data were successfully fitted by a set of three Schottky functions. The broadening of the Schottky anomaly at zero magnetic field may be an evidence of the non-equivalent sites of Nd³⁺ ions, which is probably connected with a phase segregated state of the compound. From other hand the top GSD level has to be split into a band due to the exchange interaction of the Nd magnetic system with spin-wave band states of the Mn subsystem, so the anomaly has not be described by a single Schottky function even in a single-phase crystal. Thus the number three in the fitting is a formal characteristics of the expansion used, and can be connected directly nether with a number of the coexisting crystal phases, nor with upper crystal field Kramers doublets, since the nearest one to GSD is lying about 100 K higher [5].

In the present work the effect of magnetic fields up to 9 T on the Schottky-like heat capacity anomaly of Nd₂/₃Ca₁/₃MnO₃ has been studied. It permitted to estimate the effective molecular field of Mn spin system (Hₘₙ) and GSD g-factors of Nd³⁺ ions in the compound.

2. Experiment
Ceramic samples Nd₂/₃Ca₁/₃MnO₃ were prepared by a standard solid state reaction technique from stoichiometric amounts of proper powders. X-ray crystal-structure analysis indicated a single-phase material. Heat capacity C(T) measurements were made using Quantum Design Physical Properties Measurement System (PPMS) in the 2-250 K temperature range under magnetic fields up to 9 T.

3. Results and discussion
Temperature dependent heat capacity of Nd₂/₃Ca₁/₃MnO₃ has been revealed to show a significant shoulder below about 20 K under magnetic fields up to 9 T (Figure 1). Applied magnetic field broadens the anomaly region and shifts it towards higher temperatures. The anomaly has been interpreted as a two-level Schottky-like one caused by the splitting of the ground state doublets of Nd³⁺ ion due to the exchange interaction with the Mn spin system supplemented by an applied external magnetic field (the ground state of Nd³⁺ ion, ⁴I⁹/₂, is split into five Kramers doublets by crystal field in Nd₂/₃Ca₁/₃MnO₃). The specific heat of the Nd₂/₃Ca₁/₃MnO₃ at temperatures and high magnetic fields studied represents a sum of the phonon (Debye) contribution, a contribution from the higher crystal field Kramers doublets, the contribution from spin-wave excitations, and two-level Schottky contribution. The hyperfine contribution to the specific heat caused by the local magnetic field at the Mn and Nd nucleus is negligible at temperatures above 2 K, and the linear contribution from free electrons is not present in the studied magnetic insulator. Using the method from [1], we have approximated low temperature heat capacity data in the each magnetic field studied by a sum of three Schottky functions

\[
C_{Sch}^*(T,H) = \frac{2}{3} \sum_{n=1}^{3} a_n(H) \left( \frac{\Delta_n(H)}{T} \right)^2 \frac{\exp \left( \frac{\Delta_n(H)}{T} \right)}{1 + \exp \left( \frac{\Delta_n(H)}{T} \right)}
\]

were parameters \( \Delta_n \) and \( a_n \) depend on the external magnetic field, \( R=8.314\ J/mole\cdot K \) is the universal gas constant, and the asterisk at \( C_{Sch}^* \) indicates that the value includes contributions from the higher crystal field Kramers doublets. The parameters of the equation (1) are summarized in Table 1.

| Magnetic field (T) | a₁ | a₂ | a₃ | \( \Delta_1 \) (K) | \( \Delta_2 \) (K) | \( \Delta_3 \) (K) |
|-------------------|----|----|----|-------------------|-------------------|-------------------|
| 0                 | 0.248 | 0.231 | 0.561 | 8 | 16.2 | 25 |
| 2                 | 0.248 | 0.231 | 0.64 | 9 | 17.2 | 26.7 |
| 5                 | 0.248 | 0.231 | 0.72 | 12 | 20.2 | 31 |
| 9                 | 0.248 | 0.27 | 0.8 | 18 | 28 | 40 |
It is seen that the splitting parameters $\Delta_n$ increase with applied magnetic field growth (Table 1, Figure 2). The variation of $\Delta_n$ in magnetic fields cannot be fitted linearly in contrast to [6], where antiferromagnetic insulator NdMnO$_3$ was studied. It is possibly connected with AF-F phase transition, which takes place in magnetic field about 3 T [7].

Using the equation

$$\Delta_{3(i)}(H) = \mu_B g_{(i,l)} (H_{ex} + H)$$

and the high field data for $\Delta_n(H)$, we have estimated $H_{ex} \approx 9$ T and the GSD g-factors $g_\parallel$ and $g_\perp$ as 3.4 and 2.2, respectively. These data look reasonably in comparison with those obtained in other experiments [6, 8, 9]. Here we consider, that the field $H$ exceeds a sum of a demagnetization field $H_0$ (an evaluation gives $H_0 \leq 0.75$ T at the experiment), an anisotropy field $H_a$ for the Mn magnetic subsystem (we suppose, that $H_a \leq 0.1$ T, but even if $H_a$ slightly exceeds 1 T, equation (2) remains still reasonable), and a field $H_f$ of the AFM-FM transition ($H_f \sim 3$ T [7]).

The Schottky entropy $S_{Sch}^*(\infty)$ for the approximated experimental data $C_{Sch}^*/T$ is as follows:

$$S_{Sch}^*(\infty) = 2\frac{R}{3} \ln 2 \sum_{n=1}^{3} a_n(H)$$

The sum of the coefficients $a_n$ has to satisfy the condition $\sum_{n=1}^{3} a_n = 1$. The condition is practically fulfilled under zero magnetic field, that provides the reliability of the approximation (Table 1). But the sum increases with a magnetic field applied, that is evidently connected with an additional contribution from the higher crystal field Kramers doublets. To estimate this additional contribution we have used a function

$$C_{Sch0}^*(T, H) = \frac{2}{3} R \sum_{n=1}^{3} a_n(0) \left( \frac{\Delta_n(H)}{T} \right)^2 \exp \left( \frac{\Delta_n(H)}{T} \right) \left[ 1 + \exp \left( \frac{\Delta_n(H)}{T} \right) \right]$$

where coefficients $a_n$ correspond to the situation $H=0$. The difference between functions $C^*(T, H)$ and $C_{Sch0}^*(T, H)$ roughly corresponds to contribution from the lattice, Mn magnetic system [1] and higher crystal field Kramers doublets, which was evaluated using [10] and data from [5] (figure 3).

Figure 1. Temperature dependent heat capacity of Nd$_{2/3}$Ca$_{1/3}$MnO$_3$ under magnetic fields up to 9 T.

Figure 2. Field dependences of the calculated parameters $\Delta_1$ and $\Delta_2$ in the equation (1).
Figure 3. The entropy derivative $C/T$ for the Nd$_{2/3}$Ca$_{1/3}$MnO$_3$ compound under magnetic field 9 T. Solid line (blue in color) represents approximation of the experimental data $C_{\text{exp}}(T)/T$ by a sum of three Schottky contributions; dash line (red in color) represents $C_{\text{Sch}}^*(T,H)/T$; dash-dot line (black in color) represents a difference of $C/T$ and $C_{\text{Sch}}^*(T,H)/T$.

The Nd-ions magnetic ordering was revealed below 28 K, it introduces an additional contribution to the ferromagnetic moment producing clear anomalies of the field-cooled and zero-field-cooled magnetizations of the Nd$_{2/3}$Ca$_{1/3}$MnO$_3$.

4. Conclusions
Heat capacity of Nd$_{2/3}$Ca$_{1/3}$MnO$_3$ reveals broad Schottky-like anomaly, which originates from the Nd magnetic ordering caused by the splitting of the Nd$^{3+}$ ions ground-state doublet in the effective molecular field $H_{ex}$ of Mn spin system supplemented by an applied external magnetic field. The anomalies found were fitted by a sum of three Schottky functions, that may be considered as an evidence of the presence of thermodynamically segregated structural phases in the compound, and as an effect by a broadening of the upper level of the split GSD of the Nd$^{3+}$ ion caused by the indirect exchange interaction with spin wave states of the Mn subsystem. The GSD $g$-factors $g_\parallel$ and $g_\perp$ was estimated as 3.4 and 2.2, respectively, and the effective molecular-field at Nd$^{3+}$ site $H_{ex}$ as 9 T.

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6. References
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