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LETTER

Negative magnetization in $La_{0.75}Nd_{0.25}CrO_3$ perovskite

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Introduction

Complex oxides of transition metals (TM) with the perovskite structure have attracted great interest due to a whole series of unique properties such as high-temperature superconductivity, colossal magnetoresistance, coexisting (anti)ferromagnetism, and (anti)ferroelectricity. Recently, several groups have reported negative magnetization observed below a certain temperature on cooling of a sample in a low or a medium (up to 4 kOe) magnetic field. This phenomenon was discovered for $LaVO_3$ [1], YVO_3 [2], $La_{1-x}Gd_xMnO_3$ [3], $Nd_{1-x}Ca_xMnO_3$ [4], $GdCrO_3$ [5], $La_{1-x}Pr_xCrO_3$ [6], and some others perovskites. In the present paper, we report on the reversal of the magnetization for $LaCrO_3$–$NdCrO_3$ solids.

The end compounds, $LaCrO_3$ and $NdCrO_3$, have an orthorhombic perovskite structure at room temperature (space group *Pbnm* (*Pnma*)) [7]. The exchange coupling between the magnetic moments of the Cr^{3+} ions in $LaCrO_3$ is predominantly antiferromagnetic. G-type of antiferromagnetic structure is established below the Neel temperature of $T_N = 288$ K [6]. The weak ferromagnetic moment, peculiar to $LaCrO_3$, is due to the antisymmetric Dzyaloshinskii–Moriya interaction [8, 9].

In $NdCrO_3$, the magnetic moments of Cr^{3+} ions are ordered in G_zF_x mode (in *Pbnm* space group notation) at $T_N = 214$ K [10]. Below this temperature, magnetization of the Cr sublattice induces an effective magnetic field on the Nd sublattice due to Nd–Cr interaction leading to a weak ferromagnetic ordering of the Nd^{3+} magnetic moments in C_yF_x mode [10]. At $T_R = 35$ K, a Morin-type phase transition occurs and, down to the lowest temperatures, G_y (Cr^{3+})–C_z (Nd^{3+}) antiferromagnetic structure persists [10].

The magnetic moments of rare-earth (RE) ions are polarized due to the coupling with transition-metal subsystem resulting in a noticeable anisotropic contribution to the low-temperature magnetic properties. Dilution of the rare-earth sublattice with diamagnetic ions changes strong anisotropy of RE-TM exchange, thus leading to the intriguing behavior of the magnetization. In this work, we describe magnetic properties of $La_{0.75}Nd_{0.25}CrO_3$ solid solution and discuss possible reasons for the negative magnetization appearance.

Experimental

The polycrystalline sample $La_{0.75}Nd_{0.25}CrO_3$ was prepared by a solid-state reaction method using high-purity La_2O_3, Nd_2O_3, and Cr_2O_3 reagents. Starting materials were mixed in stoichiometric proportions and heated in air at 1,000 °C for 3 h and 1,500 °C for 2 h with intermediate grinding. The unit cell parameters and the phase purity of the sample were checked by X-ray analysis using a DRON-3M diffractometer with Cu Kα radiation. The data were analyzed with the FULLPROF program. Magnetization measurements were

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performed with a MPMS-5 SQUID magnetometer (Quantum Design). Magnetization-temperature curves were measured in both zero-field-cooled (ZFC) and field-cooled (FC) modes.

Results and discussion

The room temperature X-ray diffraction analysis showed that the $La_{0.75}Nd_{0.25}CrO_3$ sample had orthorhombic cell with a = 5.4799(3), b = 5.4739(4), c = 7.7491(4) (space group *Pbnm*). No secondary or impurity phases were detected. A good agreement between the observed and calculated diffraction patterns is shown in Fig. 1.

The temperature dependence of magnetization for $La_{0.75}Nd_{0.25}CrO_3$ sample at H = 500 Oe is presented in Fig. 2. A clear transition from a paramagnetic to a magnetically ordered state is observed at T_N = 268 K. With cooling of the sample in the FC mode, the magnetization increases, reaching a maximum at 60 K, then begins to decrease, crosses zero, and takes on a negative value. Entirely different behavior of magnetization at low temperatures is observed in the case of ZFC measurement: decrease of ZFC magnetization is observed with increasing temperature to 55 K. At around 75 K, the ZFC magnetization shows a peak. As applied field increases, the negative FC magnetization disappears and strong increase of magnetization begins to develop with decreasing temperature below ~60 K (Fig. 3).

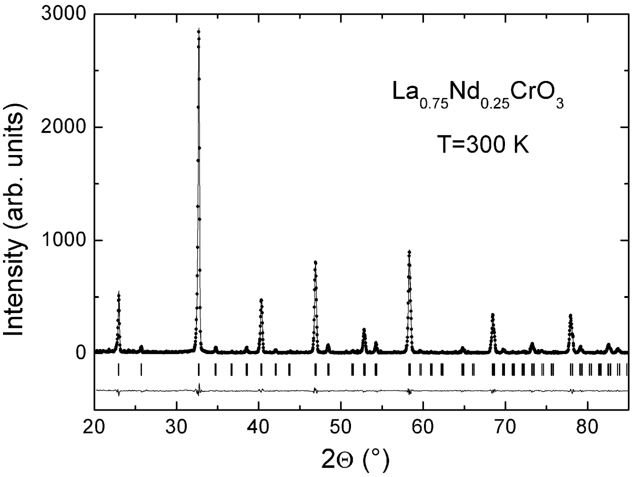

Fig. 1 Observed (solid circles) and calculated (solid line) X-ray powder diffraction patterns for the $La_{0.75}Nd_{0.25}CrO_3$ sample at T = 300 K. The difference between observed and calculated spectra is plotted at the bottom. The ticks indicate allowed Bragg peaks positions

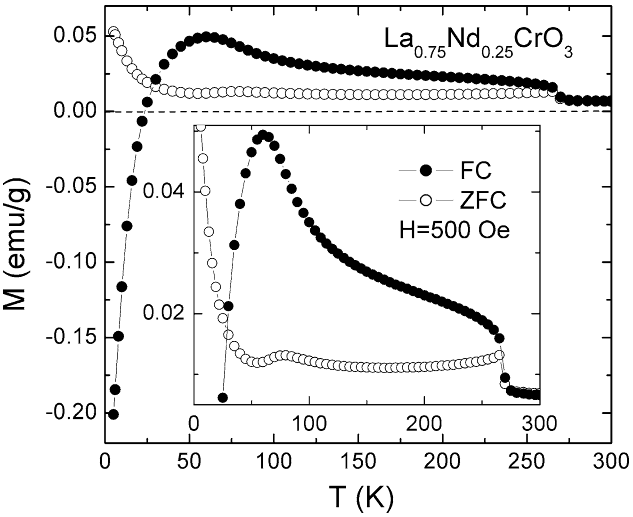

Fig. 2 Temperature dependence of the magnetization for the $La_{0.75}Nd_{0.25}CrO_3$ sample, measured at 500 Oe. Open and close symbols are used for the curves obtained in ZFC and FC modes, respectively

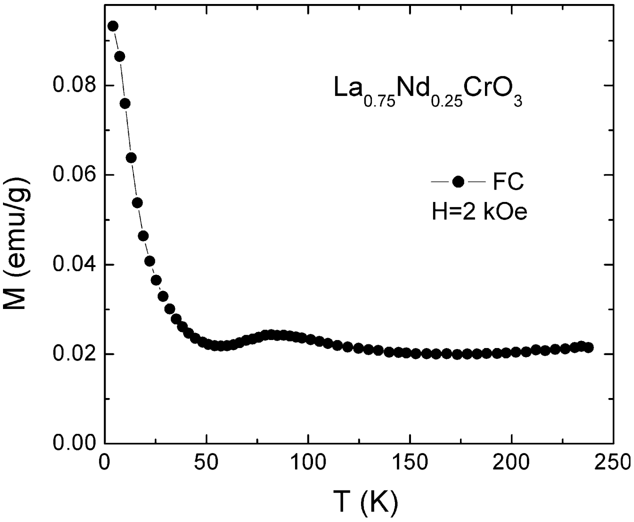

Fig. 3 Temperature dependence of the magnetization for the $La_{0.75}Nd_{0.25}CrO_3$ sample, measured at 2 kOe in FC mode

The field dependence of magnetization for $La_{0.75}Nd_{0.25}CrO_3$ is shown in Fig. 4. The sample is characterized by a very small spontaneous magnetic moment (about 0.02 μ_B per formula unit at $T = 5$ K) and a large coercive field (more than 5.5 kOe at 5 K). The value of spontaneous magnetic moment is typical for weak ferromagnets. Increase of temperature leads to decrease both of magnetization and coercive field. No metamagnetic behavior was revealed.

Negative magnetization in $La_{0.75}Nd_{0.25}CrO_3$ can arise due to the following reasons:

1. *A structural phase transition.* Such a situation seems to be realized in $LaVO_3$ orthovanadate which undergoes a transition from orthorhombic (space group *Pbnm*) to monoclinic (space group $P2_1/b11$) unit cell symmetry at T_t = 141 K < T_N = 143 K [11]. A negative net

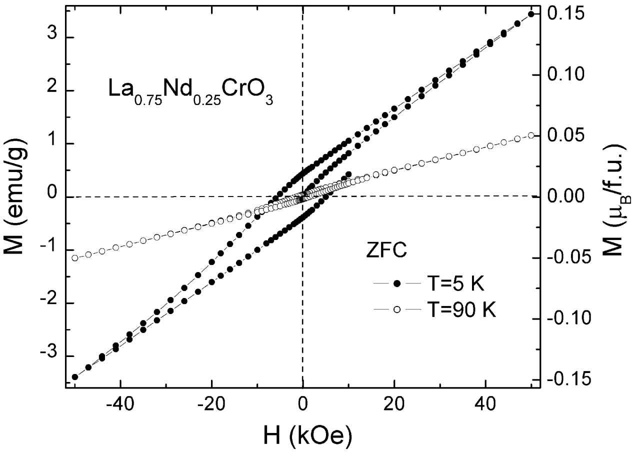

Fig. 4 Field dependence of the magnetization of the $La_{0.75}Nd_{0.25}CrO_3$ sample at different temperatures

magnetization appears below T_t [1]. The phase transition is associated with a change of both spin and orbital ordering configurations, namely, from a high temperature phase of G-type magnetic and C-type orbital ordered state to a low temperature phase of C-type magnetic and G-type orbital ordered state, causing a reversal of the net magnetization [11]. In the case of lanthanum and rare-earth orthochromites, no structure changes observed below T_N have been reported [6, 7, 12, 13].

2. *A change of sign of the f-d exchange interactions.* Reversal of magnetization observed in the lightly doped $Nd_{1-x}Ca_xMnO_3$ manganites is explained in the framework of a two-phase model according to which the samples consist of exchange coupled ferromagnetic and weak ferromagnetic phases [4]. The phases differ in the sign of the f-d exchange above effective temperature of $T_{eff} \sim 9$ K. The magnetic moments of the neodymium ions are ordered parallel to the moments of the manganese ions in the ferromagnetic phase, and opposite to the direction of the weak ferromagnetic vector at $T > T_{eff}$ in the weak ferromagnetic phase. Below T_{eff}, the reorientation of the weak ferromagnetic vector and the ferromagnetic phase in the direction of the magnetic moments of the neodymium ions in the weak ferromagnetic phase occurs, resulting in the negative magnetization appearance [4]. A change of sign of the f–d exchange leads to pronounced metamagnetic anomalies (triple hysteresis loops) [4], which are not observed for $La_{0.75}Nd_{0.25}CrO_3$ sample (Fig. 4). More importantly, no coherent magnetic contribution from the side of rare-earth ions to the neutron scattering is observed in the diffraction experiments performed for $La_{0.75}Nd_{0.25}CrO_3$ [13] and $La_{0.5}Pr_{0.5}CrO_3$ [6] compounds.
3. *Spin reorientation.* A negative net magnetization can arise due to a change of an easy direction. In $NdCrO_3$, as was mentioned above, due to strong anisotropy of Nd–Cr exchange, which stabilizes the antiferromagnetic phase G_y, the Morin-type spin reorientation phase transition G_zF_x–G_y takes place with decreasing temperature at $T_R = 35$ K [14]. The existence of the high temperature magnetic phase G_zF_x is also determined by Nd–Cr anisotropic interactions, since the magnetocrystalline anisotropy of the Cr-subsystem stabilizes the G_xF_z phase [14]. Therefore, one can expect that in $La_{0.75}Nd_{0.25}CrO_3$ solid solution, diluted with diamagnetic La^{3+} ions, high temperature phase has G_xF_z magnetic structure. With decreasing temperature, when Nd–Cr anisotropic interactions become significant, G_xF_z–G_zF_x-type phase transition can occur, leading to appearance of the negative net magnetization in a low applied field. However, neutron diffraction experiments do not confirm the existence of such a transition so far [6, 13]. (On the other hand, it is necessary to note that neutron diffraction is not a very convenient tool to reveal the spin-reorientational transition in this particular case-corresponding magnetic peaks are located almost at the same angle [6]). To verify this hypothesis, carrying out of precise investigations of the magnetic properties of $La_{1-x}Nd_xCrO_3$ single crystals is desirable.
4. *A negative coupling between sublattices of 3d and 4f ions.* The negative magnetization below certain temperature can be due to the paramagnetic effect of RE ions whose magnetic moments direction is opposite to that of canted TM ones [3, 5, 6]. Accordingly, the behavior of the magnetization observed in $La_{0.75}Nd_{0.25}CrO_3$ in a low applied field with decreasing temperature (Fig. 2) can be qualitatively explained in the following way: due to the antiferromagnetic coupling between Nd^{3+} and the canted Cr^{3+} moments, the Nd^{3+} magnetic moments are polarized antiparallel with respect to a ferromagnetic component of the chromium spins; the Nd^{3+} moments are more and more aligned in the internal field of the chromium moments as temperature decreases, yielding a negative magnetization at the lowest temperatures, when the polarization of the Nd^{3+} moments exceeds the ferromagnetic component of the Cr^{3+} sublattice. The model has been successfully applied for the explanation of the negative magnetization observed in $GdCrO_3$ [5] and $La_{1-x}Pr_xCrO_3$ [6] perovskites and seems to be consistent with the rest of the experimental observations (i.e., suppression of the negative FC magnetization with increasing external magnetic field) obtained for $La_{0.75}Nd_{0.25}CrO_3$ compound (Fig. 3). Indeed, if the applied field becomes larger than the internal field from Cr^{3+}, it would prevent the opposite alignment of the RE moments with respect to the weak ferromagnetic moment of Cr^{3+} sublattice. Thus, the negative magnetization observed for the $La_{0.75}Nd_{0.25}CrO_3$ perovskite is

not caused by any magnetic or structural phase transition and is likely explained by the paramagnetic effect of Nd^{3+} ions. It is necessary to note that even more pronounced phenomenon of the negative magnetization was also revealed in the low-field measurements carried out for $La_{0.6}Nd_{0.4}CrO_3$ and $La_{0.5}Nd_{0.5}CrO_3$ solid solutions [15]. The neutron powder diffraction measurements performed for the compounds revealed the existence of the G_z-type antiferromagnetic ordering for Cr^{3+} moments (in the temperature range $T_N < T \leq 5$ K) with no indication of the magnetic ordering for Nd^{3+} moments (at least down to 5 K). The results support the propriety of the last scenario (details will be reported elsewhere).

Conclusions

In conclusion, we investigated crystal structure and magnetic properties of $La_{0.75}Nd_{0.25}CrO_3$ solid solution. It was shown that the sample had an orthorhombically distorted perovskite structure (space group *Pbnm*). A paramagnet to a weak ferromagnet transition is observed at $T_N = 268$ K. With cooling of the sample in a low applied field of $\sim$500 Oe its net magnetization, initially oriented parallel to the field, changes sign at low temperatures. In the higher magnetic fields, this effect is suppressed. The probable reasons that might be responsible for an appearance of the reversal of the magnetization were discussed. It was shown that the observed phenomenon can be due to the paramagnetic effect of Nd^{3+} ions.

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