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# Magnetism in $NdMnO_{3+\delta}$ Studied by the Single Crystal Neutron Diffraction

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We present the single crystal neutron diffraction experiment performed on the $NdMnO_{3+\delta}$ compound. The aim of the experiment was to study/revisit the magnetic structure of the compound. We have confirmed the ordering of Mn sublattice below $T_N = 85.5$ K and confirmed that the Nd sublattice orders below $T_1 \approx 20$ K with Nd moments aligned parallel to the $b$-axis.

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The $ReTO_3$ compounds (Re = rare earth, T = Mn, Fe) attract large attention due to their very interesting physical properties e. g. multiferroicity and ferroelectricity [1], compensation temperatures [2, 3], promising application potential in the field of magnetocaloric effect at room temperature [4], nonlinear magnetooptical effects in the THz region and other physical properties.

Neutron powder diffraction (NPD) experiments performed on $NdMnO_3$ revealed that the compound orders antiferromagnetically (ordering of Mn sublattice, spin arrangement ($C_xF_y0$)) at $T_N = 82$ K [5] and exhibits another transition which corresponds with additional anomaly in AC susceptibility around $T_1 \approx 20$ K [6]. The ordering at $T_N$ is ascribed to the superexchange between Mn ions mediated by oxygen atoms [2], while the description of the transition at $T_1$ remains controversial: One group of authors claim that Nd sublattice orders ferromagnetically (moments parallel to $c$-axis) at $T_1$ as a consequence of the polarization of $Nd^{3+}$ ions by Mn ions (i.e. order–to–order magnetic phase transition) [5], while the other group of authors claim that Nd ions possess the ordered magnetic moment already below $T_N$ and effect at $T_1$ is the consequence of the segregation of the ferromagnetic clusters within the antiferromagnetic matrix [3]. It is also worth to mention that the interplay of the magnetic interactions in this type of system leads to an effect of negative magnetization and compensation temperatures if the compound is slightly non–stoichiometric ($NdMnO_{3.11}$ [2, 3]), or slightly doped ($NdMn_{0.8}Fe_{0.2}O_3$ [6], $Nd_{0.92}Ca_{0.08}MnO_3$ [7]). Since in this compound manganese ions may be in 3+ or 4+ oxidation state, the nonstoichiometry of the compound, which depends on the preparation route, is a common phenomenon [2, 7]. In our paper we have focused on study of magnetic structure, which was derived from neutron diffraction experiment performed on a single crystal.

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Single crystals of $NdMnO_{3+\delta}$ were prepared by floating zone method in an optical mirror furnace. As starting materials we have used oxides of $MnO_2$, $Nd_2O_3$ and $Fe_2O_3$ with 3N purity, which were mixed in a stoichiometric ratio, cold pressed into rods and sintered at 1200 °C for 12 hours in air. The floating zone experiments were performed using the 4-mirror optical furnace equipped with 1 kW halogen lamps. We have used pulling speed of 5 mm/h, rotation of both shafts 10 rpm and flowing (2 l/min) air atmosphere. The quality of the grown single crystals was checked on E4 two axis neutron diffractometer (Helmholtz Zentrum Berlin). It was found that the crystal has only the moderate quality with several sub–grains miss–oriented by roughly 0.75°. The oxygen nonstoichiometry ($\delta$) was estimated by the iodometric titration and has value of about $\delta = 0.02$. The neutron diffraction experiment was performed on E4 diffractometer, using the standard Orange cryostat and neutron wavelength of 2.432 Å. During the experiment we have studied 21 different reflections in the temperature range 1.6 – 100 K.

All observed reflections were indexed by integer h, k, l indexes. No change in $2\theta$ and $\omega$ during the temperature scans was observed. This suggests that the magnetic unit cell is identical with the crystallographic unit cell [magnetic $\boldsymbol{k}$ vector equal to (0 0 0)] and that the crystal structure of the material does not change. Integrated intensities of the studied reflections can be divided into three groups: i) intensity keeps constant value or changes only slightly in the whole temperature range (Fig. 1a), ii) intensity increases below $T_N \approx 80$ K (Fig. 1b) and iii) intensity is constant at temperatures higher than $T \approx 30$ K, but at lower temperatures increases (Fig. 1c).

Neutron diffraction experiment performed on a single crystal revealed that reflections (010) (Fig. 1b) and (200) (Fig. 2) gain the intensity by cooling down below 80 K. We assign this extra intensity to the ordering of Mn sublattice ($T_N$ =85.5(2) K [6]). At $T_N$ we have observed no increase of the intensity on (002) reflection (Fig. 1c) within the experimental error. These results are completely in agreement with NPD data published by Muñoz

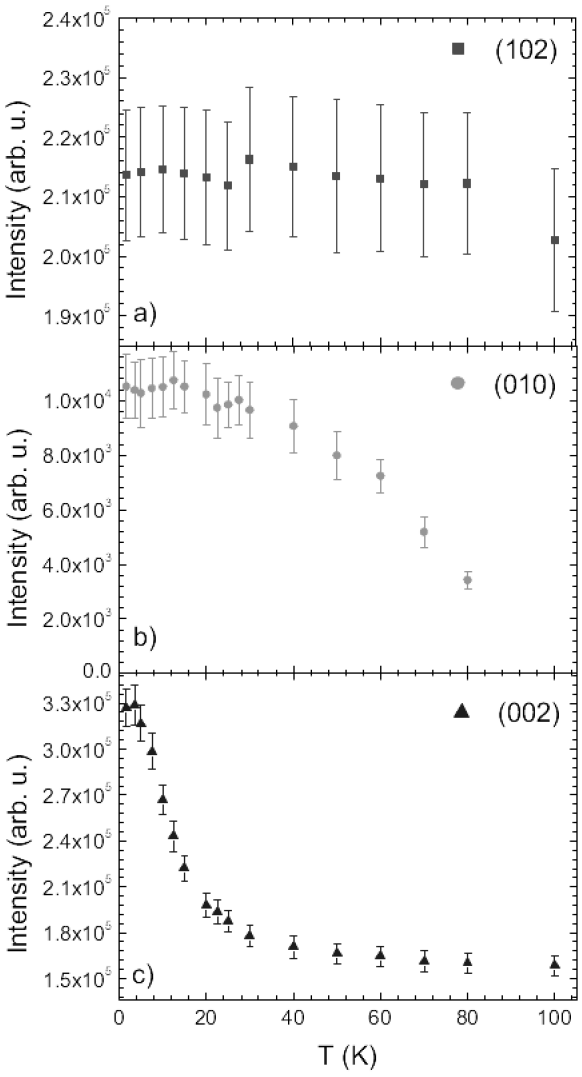


Fig. 1. Representative set of the observed reflections. The intensities are normalized to the same monitor. Note, that we index reflections using the space group *Pnma*; and lattice parameters: $a = 5.838$ Å, $b = 7.547$ Å, $c = 5.414$ Å.

et al. [5]. Additionally, some reflections, like (002) (see Fig. 1c), or (200) (Fig. 2) gain intensity below 25–30 K, which we ascribe to the order-to-order magnetic phase transition. Following Muñoz et al. [5] we estimate that the Nd sublattice orders along the *b*-axis, since (010) reflection (Fig. 1b) does not gain the intensity within the experimental error.

In conclusion, for the first time the magnetic structure of $NdMnO_{3+\delta}$ was studied on a single crystal. Our investigation confirmed results, which have been already obtained by neutron powder diffraction [5]. The antiferromagnetic ordering, which was observed below the Néel temperature $T_N = 85.5$ K [6], can be attributed to the ordering of Mn sublattice. The order-to-order magnetic phase transition was observed below 25 K. This transition we attribute to the ordering of Nd sublattice with magnetic moments oriented along the *b*-axis.

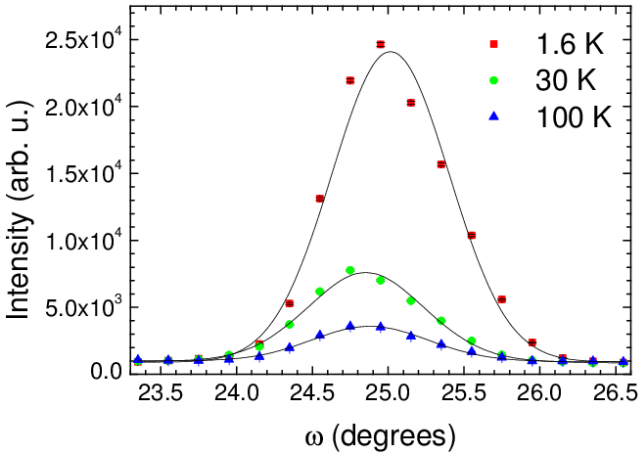


Fig. 2. The $\omega$ scans through the (200) reflection at various temperatures. The lines are the best fits using the Gaussian function.

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## References

[1] H. Kuwahara, K. Noda, J. Nagayama, S. Nakamura, *Phys. B* **359 – 361**, 1279 (2005).

[2] F. Bartolomé, J. Bartolomé, J. Campo, *Phys. B* **312–313**, 769 (2002).

[3] F. Bartolomé, J. Herrero-Albillos, L.M. García, J. Bartolomé, N. Jaouen, A. Rogalev, *J. Appl. Phys.* **97**, 10A503 (2005).

[4] X. Moya, L.E. Hueso, F. Maccherozzi, A.I. Tovstolytkin, D.I. Podyalovskii, C. Ducati, L.C. Phillips, M. Ghidini, O. Hovorka, A. Berger, M.E. Vickers, E. Defay, S.S. Dhesi, N.D. Mathur, *Nat. Mater.* **12**, 52 (2013).

[5] A. Muñoz, J.A. Alonso, M.J. Martínez–Lope, J.L. García-Muñoz, M.T. Fernández–Díaz, *J. Phys.: Condens. Matter* **12**, 1361 (2000).

[6] M. Mihalik jr., M. Mihalik, J. Lazúrová, M. Fitta, M. Vavra, *EPJ Web of Conferences* **40**, 15007 (2013).

[7] I.O. Troyanchuk, V.A. Khomchenko, G.M. Chobot, A.I. Kurbakov, A.N. Vasil'ev, V.V. Eremenko, A.V. Sirenko, M.Yu. Shvedun, H. Szymczak, R. Szymczak, *J. Phys.: Condens. Matter* **15**, 8865 (2003).