NATIONAL RESEARCH CENTRE
«KURCHATOV INSTITUTE»

PETERSBURG NUCLEAR PHYSICS INSTITUTE
Russia, 188300, Leningrad District , Gatchina, Orlova Roscha

Magnetic phase separation in oxygen-deficient double perovskite $Sr_2MnNbO_{6-\delta}$

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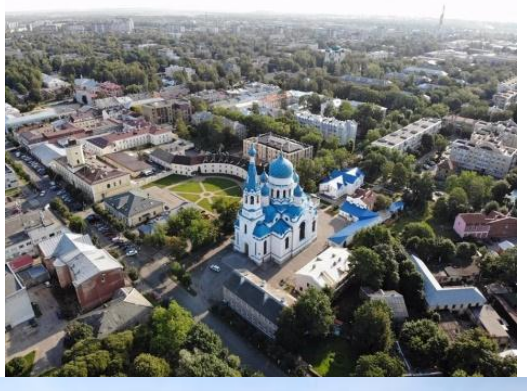
Gatchina,
Russia,

located 45 km south of St. Petersburg, former residence of Russian emperors



List of participants

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Tatiana Chupakhina **Julia Deeva** **Vladimir Shustov**	*Institute of Solid State Chemistry (Ekaterinburg), RUSSIA*
Tanmoy Maiti	*Department of Materials Science and Engineering Indian Institute of Technology(Kanpur), INDIA*

Motivation for my talk

Un unusual magnetic ordering in double perovskites → *well known and studied in sufficient detail*

The most interesting properties appear when the compounds under study ($Sr_2MnNbO_{6-\delta}$) turn out to be oxygen-deficient

A deviation from stoichiometric composition, leads to variable valence of manganese ions with the existence of ions with different spins, Mn^{4+} ($S = 3/2$), Mn^{3+} ($S = 2$), and Mn^{2+} ($S = 5/2$) ions that is very unusual.

Unfortunately, it is much more difficult to study ferromagnetic ordering, as in our case, by neutron diffraction, both powder and single crystal, than antiferromagnetic ordering.

When antiferromagnetic order is established, additional peaks appear in the neutron diffraction pattern, usually in the region of small diffraction angles, often at angles smaller than the first nuclear reflections. They are easily recorded and analyzed.

With ferromagnetic ordering, additional peaks do not appear, but additional contributions to the existing nuclear reflections appear. Typically, these contributions are low in intensity, so it is necessary to use **neutron diffractometers with high aperture ratio.** To analyze this additional magnetic scattering, it is necessary to determine which nuclear reflections they are added to, i.e. we need **a high resolution diffractometer.**

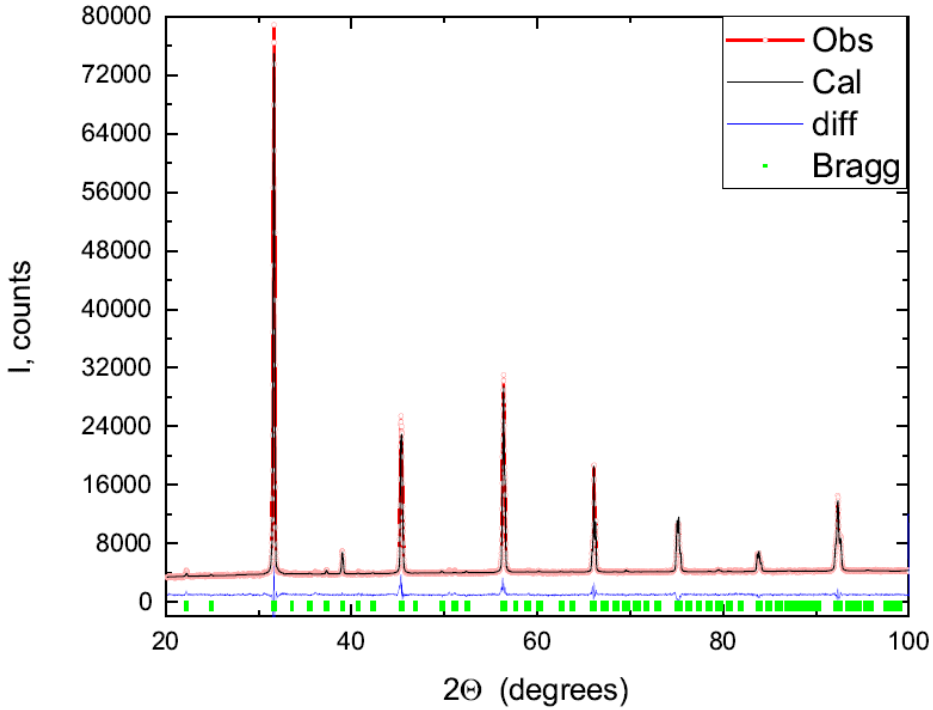
All of this explains why we decided to turn to Chinese scientists to carry out neutron experiments. In our opinion, your instrumentation is ready to solve such complex scientific problems. We believe that the **HIPD** installation at the CARR reactor is suitable for solving the tasks set as the main device.

Structural Analysis of $Sr_2MnNbO_{6-\delta}$

Sr (Z= 38) $b_n = 0.702 \times 10^{-12}$ cm, **Nb** (Z= 41) $b_n = 0.705 \times 10^{-12}$ cm
Mn (Z= 25) $b_n = -0.373 \times 10^{-12}$ cm, **O** (Z= 8) $b_n = 0.580 \times 10^{-12}$ cm

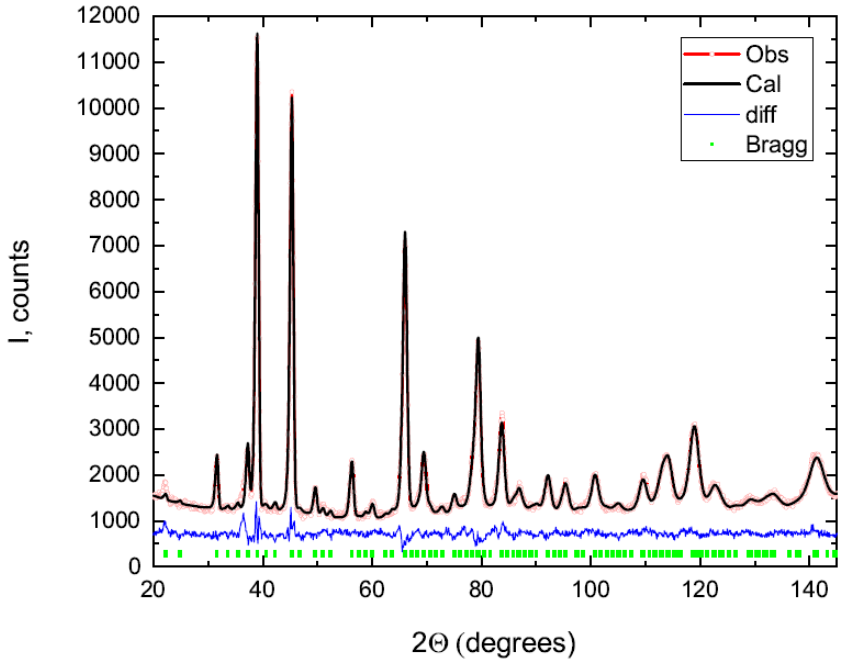
$r_{Sr} = 1.50$ Å, $r_{Nb} = 0.78$ Å,
$r_{Mn} = 0.785$ Å, $r_O = 1.28$ Å

X-Ray



Neutrons

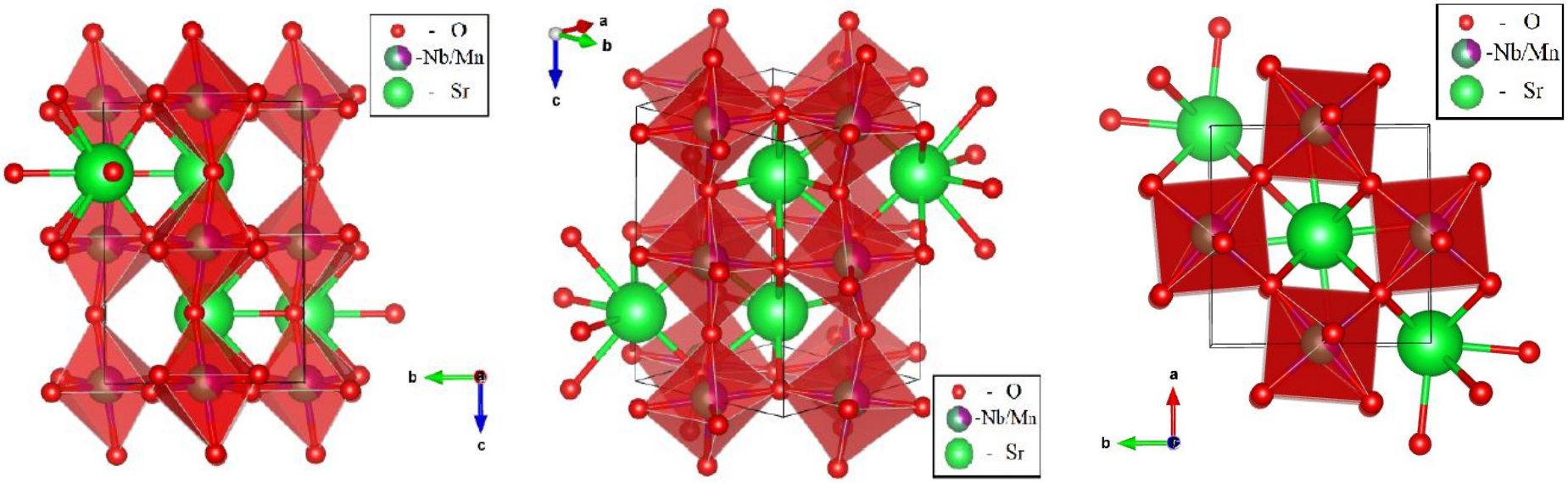
DISK diffractometer at KI, Moscow



Theoretical, experimental, and difference diffraction patterns of double perovskite $Sr_2MnNbO_{6-\delta}$ at **300 K**

Structural Analysis of $Sr_2MnNbO_{6-\delta}$

r_{Sr} = 1.50 Å, r_{Nb} = 0.78 Å,
r_{Mn} = 0.785 Å, r_O = 1.28 Å



Structure of $Sr_2MnNbO_{6-\delta}$ double perovskite

and

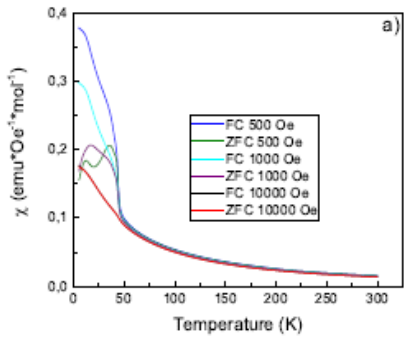
X-ray fluorescence analysis (XFA) of $Sr_2MnNbO_{6-\delta}$

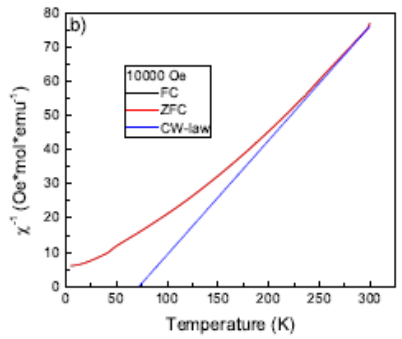
Point	Sr	Nb	Mn	Mn^{2+}	Mn^{3+}	Mn^{4+}
1.1	2	1.10	0.81	0.38	0.43	0
1.2	2	1.02	0.71	0	0.39	0.32
1.3	2	1.05	0.79	0.07	0.72	0
1.4	2	1.08	0.95	0.70	0.25	0
1.5	2	1.08	0.95	0.70	0.25	0
2.1	2	1.03	0.78	0	0.72	0.06
2.2	2	1.02	0.79	0	0.71	0.08
2.3	2	1.06	0.79	0.12	0.67	0
2.4	2	0.94	0.59	0	0	0.59
2.5	2	1.10	0.81	0.38	0.43	0
Fig. 2a	2	1.03	0.80	0	0.80	0

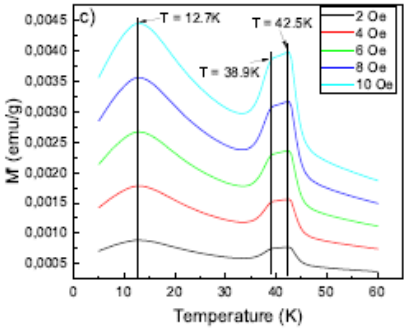
Relations between elements in $Sr_2MnNbO_{6-\delta}$

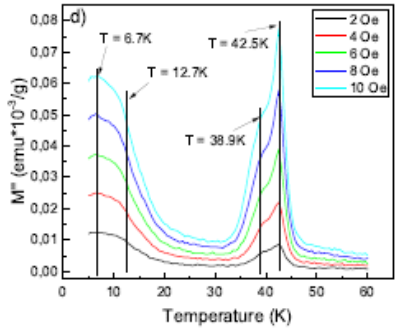
$\delta = 0.22$

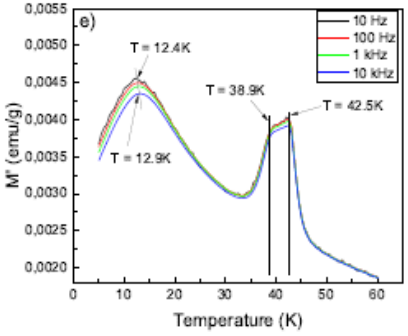
Temperature dependencies of the magnetic susceptibility and the AC magnetization of $Sr_2MnNbO_{6-\delta}$

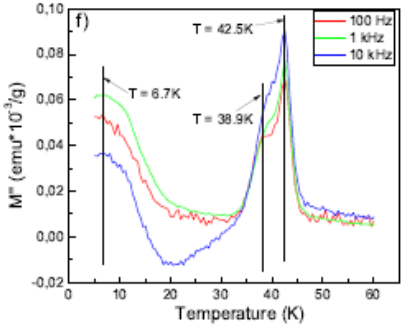












$$\chi = \frac{C}{T - \Theta_{CW}}$$

Curie-Weiss law

T_c = 42 K, Θ_{CW} = **+**72 K, C = 3.0 (K·emu/mol)

$$\Omega = \frac{T_2 - T_1}{T_2(log\nu_2 - log\nu_1)}$$

Mydosh parameter

0.0056

T_2 and T_1 are the peak temperatures at frequencies ν_2 and ν_1

The experimental magnetic moments were obtained using the equation

$$\mu_{eff} = \sqrt{\frac{3k \cdot C}{N_A}}$$

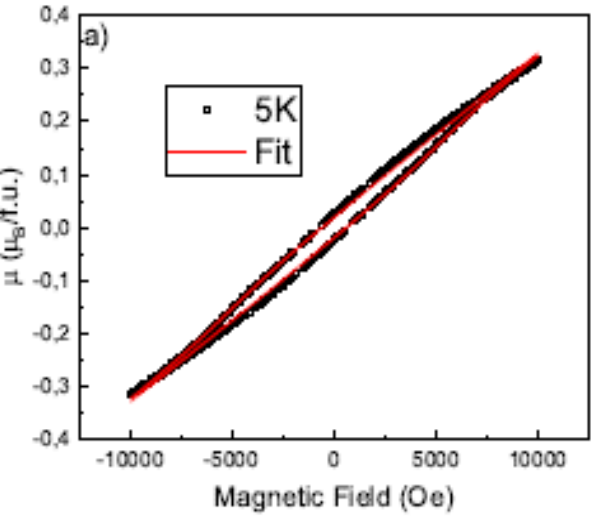
4.9 μ_B

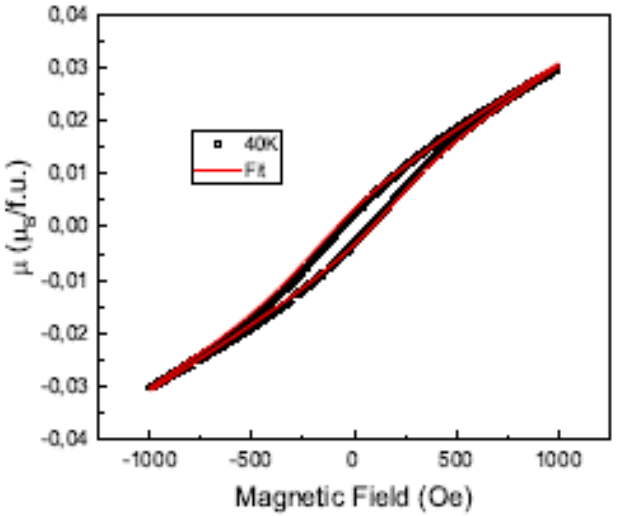
The theoretical magnetic moments were calculated assuming that the structure is ideal and the spin of magnetic ions Mn^{3+} is equal to S = 2 as

$$\mu_{eff}^{Theor} = g \cdot \sqrt{\sum [N \cdot S(S+1)]}$$

4.89 μ_B

Magnetization hysteresis loops in $Sr_2MnNbO_{6-\delta}$





FM double exchange interaction Mn^{3+}-O-Mn^{4+}

AFM superexchange interaction Mn^{3+}-O- Mn^{3+}

AFM exchange interactio Mn^{2+} -O- Mn^{3+}

Magnetization hysteresis loops in $Sr_2MnNbO_{6-\delta}$ at (a) 5K and (b) 40K

The magnetization isotherms were approximated by the sum of ferromagnetic M_F and paramagnetic M_P contributions

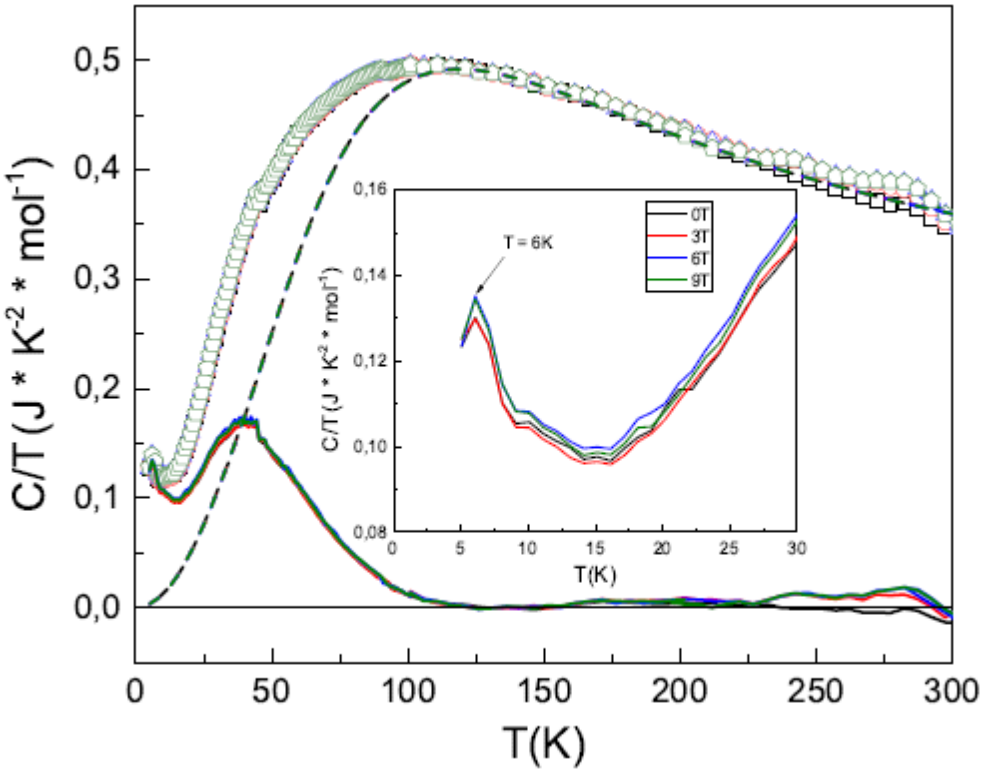
$$M_F = \frac{2 \cdot B_S}{\pi} \cdot tan^{-1}\left[\frac{(H \pm H_C)}{H_T}\right],$$

$$M_P = \chi \cdot H,$$

where
B_S *is the saturation magnetization,*
H_C *is the coercive force,*
H_T *is the internal local one-axis anisotropy field.*

$T(K)$	$B_S(emu/mol)$	$H_C(Oe)$	$H_T(Oe)$	$\chi(emu \cdot Oe^{-1} \cdot mol^{-1})$
5	150	5000	2500	0.17
15	150	2100	1200	0.16
30	150	1000	700	0.118
40	20	200	250	0.127
	30	90	250	
42	25	125	250	0.113
	25	75	250	

Temperature dependence of the specific heat of $Sr_2MnNbO_{6-\delta}$



Temperature dependence of the specific heat and its fit using Eqs. (solid line)

The experimental data was approximated via acoustic and optical phonon contributions as

$$C = \alpha_D C_D + \sum_i \alpha_{E_i} C_{E_i}$$

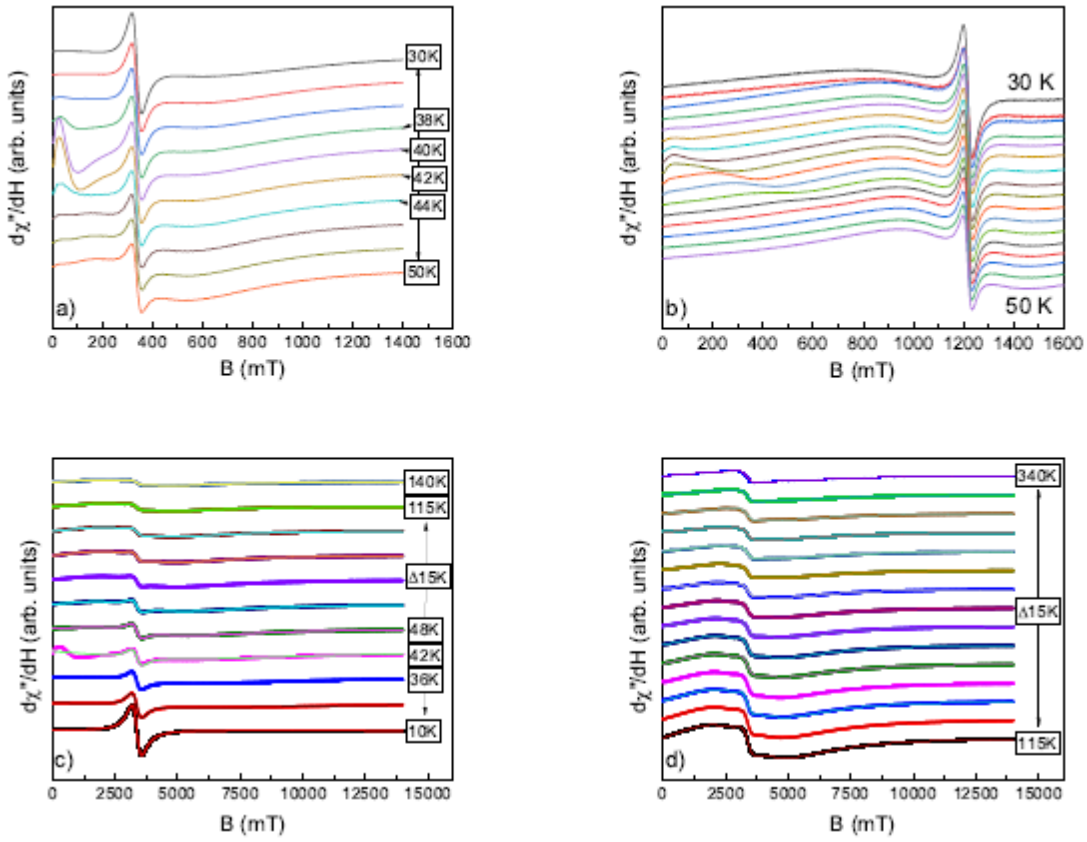
where
C_D is the Debye specific heat term and C_E is the Einstein specific heat term, which can be calculated as

$$C_D = 9R\left(\frac{T}{\Theta_D}\right)^3 \int_0^{\frac{\Theta_D}{T}} \frac{x^4 dx}{(e^x - 1)^4}$$

$$C_E = 3R\left(\frac{\Theta_E}{T}\right)^2 \frac{exp(\frac{\Theta_E}{T})}{[exp(\frac{\Theta_E}{T}) - 1]^2}$$

where
Θ_D is the Debye temperature,
Θ_E is the Einstein temperature,
R is an ideal gas constant

ESR measurements of $Sr_2MnNbO_{6-\delta}$



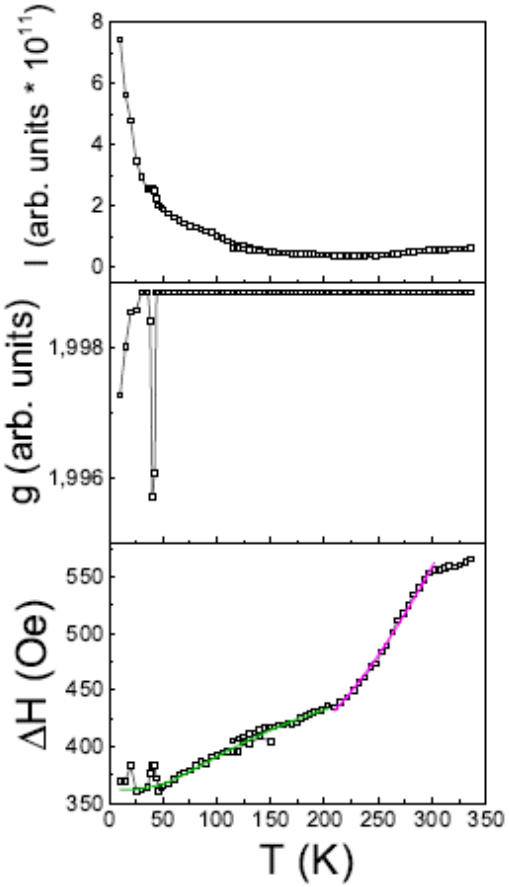
The experimental ESR spectra were approximated by the sum of two separate lines whose profile was determined by the expression

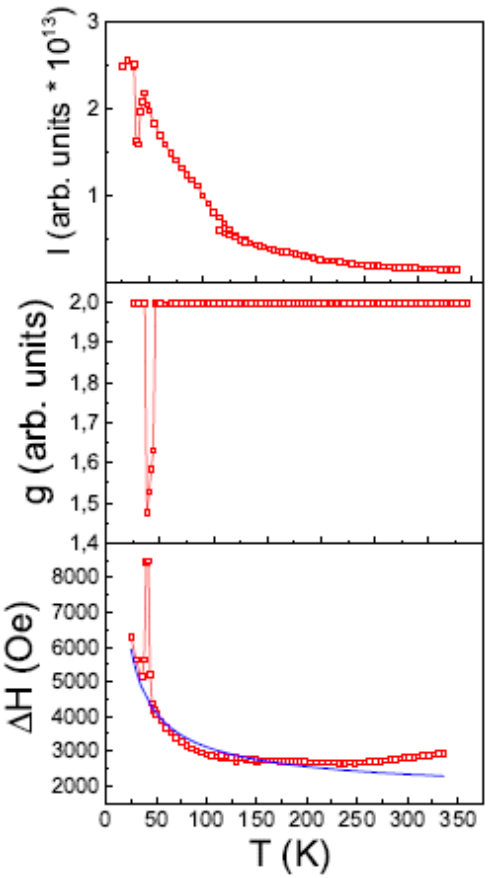
$$\frac{dP}{dH} = \frac{d}{dH}\left(\frac{\Delta H + \alpha(H - H_{res})}{(H - H_{res})^2 + \Delta H^2} + \frac{\Delta H - \alpha(H - H_{res})}{(H + H_{res})^2 + \Delta H^2}\right)$$

where

H_{res} is the resonance line position, ΔH is the linewidth, α is the asymmetry parameter which is equal to zero for $Sr_2MnNbO_{6-\delta}$.

ESR measurements of $Sr_2MnNbO_{6-\delta}$





Temperature dependencies of intensity, resonance fields, and linenwidth of the ESR lines in $Sr_2MnNbO_{6-\delta}$.
The black line is fitted by green and magenta lines via Eq.(1). The red line is fitted by the blue line via Eq. (2)

first ESR linewidth ΔH can be approximated in the 10–300K range as

$$\Delta H = \Delta H_{0i} + A_i \cdot exp\left(\frac{-2D_i}{T}\right)$$

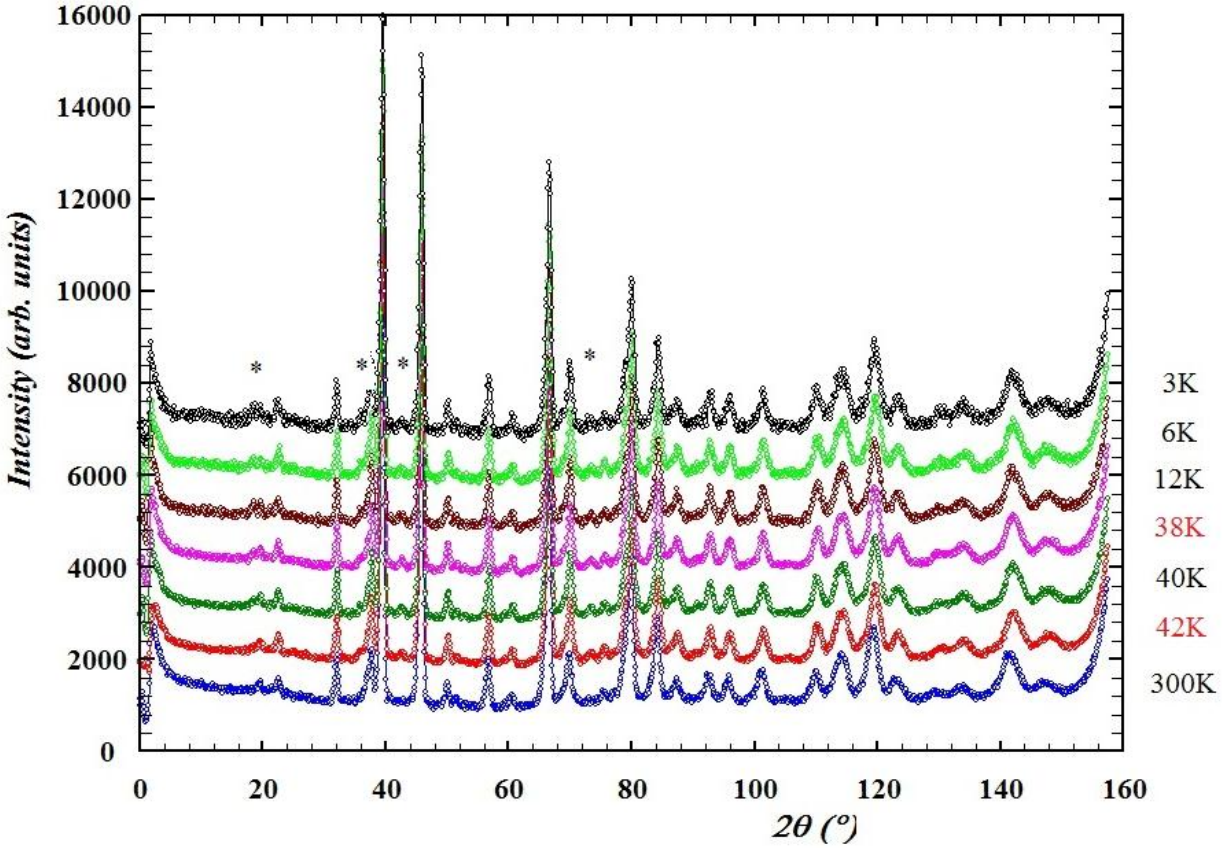
where
ΔH_{0i} is the residual width, A_i is the prefactor, and D_i is the energy gap

The temperature dependence of the second ESR linewidth ΔH was approximated by the formula for the antiferromagnetic ordering

$$\Delta H = \Delta H_{03} + A_3 \cdot \left[\frac{T_N}{(T - T_N)}\right]^{2/3}$$

where
ΔH_{03} is the residual width,
A_3 is the prefactor,
T_N is the transition temperature

$Sr_2MnNbO_{6-\delta}$



Neutron diffraction patterns of double perovskite $Sr_2MnNbO_{6-\delta}$, measured in the temperature range 3 - 300 K on a DISC diffractometer at the Kurchatov Institute, Moscow

Conclusions

Deviation from stoichiometric composition leads to a variable valence of manganese ions with the existence of ions with different spins, Mn^{4+}(S=3/2), Mn^{3+}(S=2), and Mn^{2+}(S=5/2) ions. The magnetization data of $Sr_2MnNbO_{6-\delta}$ revealed several phase transitions: to the Yafet–Kittel phase at $T_N \approx 42.5$ K, then to the incommensurate phase at $T_1 \approx 38.9$ K and two spin-reorientation transitions at $T_2 \approx 12.7$ K and, finally, also at $T_3 \approx 6.7$ K in zero magnetic field. The presence of phase transitions at these temperatures is confirmed by the different temperature dependence of the three ESR linewidths, the magnetic contribution to the specific heat capacity and AC magnetization.

Neutron powder diffraction data obtained on the DISK diffractometer at KI, Moscow were recorded two temperature points: $T \approx 42$ K, when neutron magnetic scattering of ferromagnetic type appears and $T = 38$ K, at which magnetic scattering changes (a little) its appearance. It was not possible to register other temperature features on the DISK.

New neutron studies of $Sr_2MnNbO_{6-\delta}$ and other related compounds with different TMs are proposed using neutron diffractometers in China.

my main point

Conducting the first experiments on our samples will be useful not only for physical research, but also for understanding the ways of further joint cooperation by Chinese and Russian scientists.

THANK YOU FOR YOUR ATTENTION