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Study of $Pr_{1-x}Mn_{1+x}O_3$ Perovskites

EMIL POLLERT AND ZDENĚK JIRÁK

Institute of Physics, Czechoslovak Academy of Science, Na Slovance 2,
180 40 Praha 8, Czechoslovakia

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The structural and magnetic properties of the $Pr_{1-x}Mn_{1+x}O_3$ perovskites were studied. The increase of x (i.e., $Pr/Mn < 1$) leads to the decrease of the orthorhombic deformation and of the Néel temperature and, simultaneously, to an increase of the ferromagnetic contribution. The latter effect is explained from the suggested distribution of the cations $(Pr^{3+}_{1-x}Mn^{2+}_{x})_A(Mn^{3+}_{1-x}Mn^{4+}_{x})O^{2-}_{3}$ by the double exchange of Mn^{3+}–Mn^{4+} pairs at the B—sublattice.

Introduction

The mixed oxides of the general formula $RMnO_3$, where R is an ion of the rare earth from La^{3+} to Dy^{3+}, belong to the group of orthorhombically distorted perovskites. The structural and magnetic properties of one of these compounds, namely $PrMnO_3$, were studied previously by several authors. Quezel-Ambrunaz (*1*) determined its crystal structure (space group *Pbnm*, $a = 5.545$, $b = 5.787$, $c = 7.575$) and by neutron diffraction analysis he found an antiferromagnetic ordering of the A_y-layer type below 91 K with magnetic moment $3.54\,\mu_B$ per manganese ion. Pauthenet and Veyret (*2*) report on the influence of the annealing procedure on the magnetic properties. They found for some samples ferromagnetic contribution obviously connected with an oxygen nonstoichiometry. Vickery and Klann (*3*) attempted to prepare perovskite phase containing an excess of manganese ions, i.e., substitute the small cations into the A-sublattice. Unfortunately, the samples were, probably, not a single phase so that no conclusions can be drawn from their results.

In the present work, the single phase polycrystalline samples $Pr_{1-x}Mn_{1+x}O_3$ series were prepared and a structural and magnetization study was carried out.

Experimental

Preparation of Samples

The starting materials, manganese carbonate "Baker analyzed" and praseodym oxide "Fluka puriss," tested by chemical analysis, were mixed in appropriate ratios, preheated at 800°C, pressed into pellets, and then heated 24 hr at 1400°C in air.

The diffractometer DRON-1 (USSR) using Cr$K\alpha$ radiation filtered by vanadium filter was employed for the phase analysis and the lattice parameters determination.

In the prepared samples the oxygen stoichiometry, i.e., deviations from the ideal ratio 2 : 3 between cations and oxygen anions due to the variability of manganese and/or praseodymium valencies was deter-

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mined by the chemical analysis. The classical Gorter's method (*4*) for the determination of the oxygen nonstoichiometry in ferrites, modified by Novák and Coufová (*5*), was used.

Positional parameters and distribution of cations in the perovskite structure were determined by the neutron diffraction technique. The powder diffraction patterns (see Fig. 1) were taken on the samples with $x = 0.03$ and 0.08 by means of the KSN-2 diffractometer using a Cu(200) monochromator and neutron wavelength $\lambda = 1.36$ Å. The integrated intensities and their estimated standard deviations were obtained by separating, where possible, the diffraction lines by means of a least-squares method assuming linear or exponential background and Gaussian peak shape. The positions and widths of very weak or poorly resolved lines were fixed according to positions and widths of other lines. The separated intensities together with intensities for groups of unresolved lines were processed by a refinement technique minimizing

$$R_w^2 = \Sigma \left(\frac{I_{obs} - I_{cal}}{\delta I_{obs}}\right)^2 \Big/ \Sigma \left(\frac{I_{obs}}{\delta I_{obs}}\right)^2.$$

The scattering lengths used were 0.44, −0.372, and 0.58 (× 10^{-12} cm) for Pr, Mn, and O, respectively.

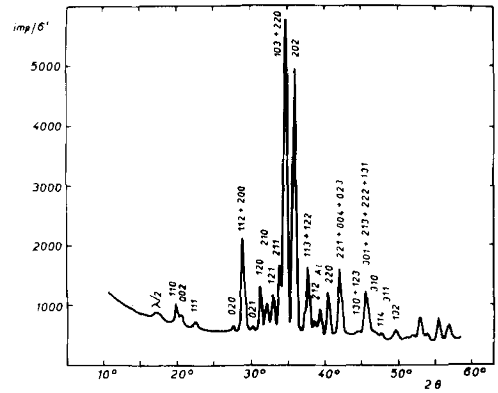

FIG. 1. The neutron diffraction pattern of $Pr_{0.92}Mn_{1.08}O_3$.

The magnetic properties of the compositions with $x = 0$, 0.05, and 0.08 have been investigated in the temperature range 4–350 K. The Faraday balance was used for the determination of the temperature dependence of the magnetic susceptibility in the paramagnetic region. The vibrational magnetometer for magnetization measurements below the magnetic ordering temperature was used.

TABLE I

COMPOSITION, X-RAY, AND MAGNETIC DATA IN $Pr_{1-x}Mn_{1+x}O_{3+\gamma}$ SYSTEM

Composition		Lattice parameters[a]								
x	γ	a (Å)	b (Å)	c (Å)	D[b]	Distribution of cations	C_{mes}	C_{cal}	T_N (K)	θ (K)
0	0.017	5.447	5.809	7.585	3.22	$(Pr^{3+}_{0.995})_A[Mn^{3+}_{0.965}Mn^{4+}_{0.03}]_B$	4.56	4.55	95	−12
0.03	0.03	5.445	5.766	7.592	2.87					
0.05	0.00	5.445	5.747	7.597	2.71	$(Pr^{3+}_{0.95}Mn^{3+}_{0.05}]_B$	4.69	4.69	84	25
0.08	0.00	5.442	5.710	7.608	2.40	$(Pr^{3+}_{0.92}Mn^{2+}_{0.08})_A[Mn^{4}_{0.08}]_B$	4.72	4.73	70	54

[a] Standard deviation of the lattice parameters a, b, c was 0.002 Å.

[b] D is a mean distortion of the lattice, given by the expression

$$D = \frac{1}{3}\sum_{i=1}^{3}\left|\frac{a_i - \bar{a}}{\bar{a}}\right| \cdot 100,$$

where $\bar{a} = (abc/4)^{1/3}$ and $a_1 = a/2^{1/2}$, $a_2 = b/2^{1/2}$, $a_3 = c/2$.

Results and Discussion

The real composition of the prepared perovskite phases resulting from the chemical analysis of the oxygen stoichiometry and their lattice parameters are given in Table I. An "excess of the oxygen" determined for the two first samples means in fact the existence of cation vacancies in the structure. The lattice parameters of the $PrMnO_3$ perovskite differ slightly from those reported earlier (*1*). Substitution of praseodymium by manganese ions decreases the orthorhombic distortion and it is seen that $x \sim 0.08$ is the limiting composition for the existence of the perovskite phase. Further increase of manganese concentration leads to the separation of the Mn_3O_4 phase while the lattice parameters of the perovskite phase remain constant.

Several models of the distribution of cations were checked on the basis of our neutron diffraction experiments. The assumptions that excessive manganese ions are precipitated or that all manganese ions are in B-sites with some A-sites remaining vacant led to rather high R_w values. Hence, these possibilities seem to be excluded. A good consistency was achieved supposing that manganese ions replace the praseodymium ions at the A-sites. The structural refinement included the positional parameters, the overall temperature coefficient B_{overall} and the mean scattering length for A-sites, from which the number of manganese ions in A-sites was then determined. As seen in Table II, this number corresponds very well to the excess of manganese ions expressed by chemical formula ($x_{\text{neutr. diffr.}} \sim x$). The comparison of observed and calculated intensities is given in Table III.

The temperature dependences of the inverse susceptibility presented in Fig. 2 exhibit a behavior typical for antiferromagnetic ordering. The Néel temperatures T_N decrease with increasing x. The ordering is accompanied by the onset of weak ferromagnetic moment which increases with x (see Fig. 3).

To interpret the magnetic data, it is necessary to know the cation valencies distribution for the individual compositions with $x > 0$. From steric reasons one may expect that manganese ions in the A-sites are bivalent and a corresponding number of those

TABLE II

NEUTRON DIFFRACTION DATA IN $Pr_{1-x}M_{1+x}O_{3+\gamma}$ SYSTEM

x_{nominal}	0.00[a]	0.03	0.08
$x_{\text{neutron diffraction}}$	—	0.032(13)	0.071(9)
Positional parameters			
A(4c)x	0.008	−0.016(4)	−0.011(2)
y	0.064	0.059(2)	0.052(2)
z	0.25	0.25	0.25
B(4b) x	0.5	0.5	0.5
$y = z$	0	0	0
O_I(4c) x	0.075	0.082(3)	0.081(1)
y	0.476	0.481(1)	0.483(1)
z	0.25	0.25	0.25
O_{II}(8d) x	−0.295	−0.286(1)	−0.287(1)
y	0.331	0.315(1)	0.315(1)
z	0.046	0.043(1)	0.043(1)
B_{overall} (Å^2)		0.03 (9)	0.3 (7)
R_w		0.037	0.071

[a] Quezel-Ambrunaz (*1*).

TABLE III

OBSERVED AND CALCULATED INTENSITIES OF DIFFRACTION LINES IN $Pr_{1-x}Mn_{1+x}O_{3+\gamma}$

	$x = 0.03$		$x = 0.08$	
hkl	I_{obs}	I_{cal}	I_{obs}	I_{cal}
110	240	231	157	172
002	116	117	108	83
111	59	60	46	29
020	38	40	36	36
112		565	787	546
200	790	215		199
021		5	21	10
120	368	390	329	359
210	170	166	208	160
121	286	277	279	254
103	2920	687	2551	626
022		2244		1983
202	2258	2201	1973	1903
113	783	154	682	115
122		653		549
212	125	131	115	119
220	344	391	329	361
221		146		101
004	708	278	513	242
023		244		192
130	93	8	73	6
123		76		64
301		177		184
213	637	131	528	100
222		95		83
131		242		160
310	74	75	64	55
114	59	72	47	49
311	64	71	42	56
132	121	134	92	101
024			15	4
312				24
230				1
204			51	8
223				77
320				170
231			259	69
124				48
321			63	58
214				33
303				5
133			210	78
105				168
232			37	33

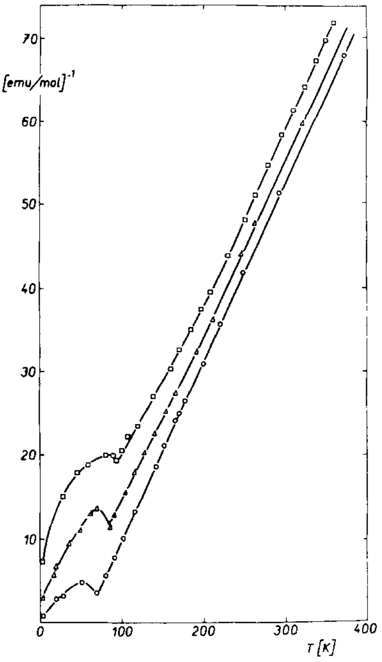

FIG. 2. The temperature dependences of the inverse susceptibility. □, $x = 0$; △, $x = 0.05$; ○, $x = 0.08$.

in the B-sites are tetravalent. The suggested distribution, neglecting oxygen nonstoichiometry, is, therefore, $(Pr^{3+}_{1-x}Mn^{2+}_x)_A(Mn^{3+}_{1-x}Mn^{4+}_x)_BO^{2-}_3$. This distribution is also supported by the close agreement between the high temperature Curie constants determined from the susceptibility measurements and those calculated on the basis of the spin-only values of the magnetic moments for Mn^{2+}, Mn^{3+}, and Mn^{4+} and the free ion value of the magnetic moment for Pr^{3+} (see Table I). For lower temperatures, the values of the observed Curie constants slightly decrease which can be explained by deviations of the effective Pr^{3+} magnetic moment from its free ion value. Then, according to the proposed distribution for the composition $x = 0, 0.05$, and 0.08, 3, 5, and 8% of manganese ions in B-sites are tetravalent. The existence of nonlocalized Mn^{3+}–Mn^{4+} pairs leads via double exchange to ferromagnetic interactions between B-cations competing with the

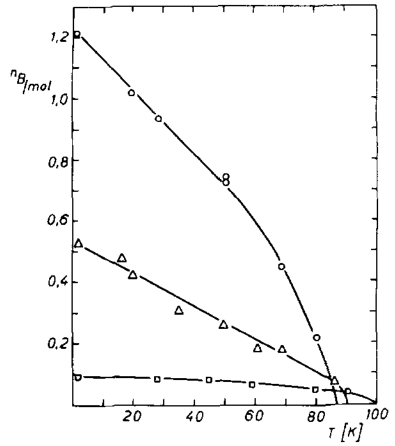

FIG. 3. The temperature dependences of the spontaneous magnetization. □, $x = 0$; △, $x = 0.05$; ○, $x = 0.08$.

antiferromagnetic superexchange between the [001] layers. In this case the theory predicts, in agreement with our experiments, the canted structure with ferromagnetic component increasing with Mn^{4+} concentration (*6*). For our composition with $x = 0$ and 0.05 the temperature T_c, for which the ferromagnetic moment arises, coincides within the experimental errors with the Néel temperature T_N similarly as it was found in $LaMnO_3$ (*7*). For the composition of $x = 0.08$, there are high-temperature ferromagnetic and low-temperature canted phases ($T_c > T_N$). The same situation was observed by neutron diffraction in $Pr_{0.9}Ca_{0.1}MnO_3$ perovskite, having a close Mn^{4+} concentration (*8*).

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