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2002 J. Phys.: Condens. Matter 14 1061

(http://iopscience.iop.org/0953-8984/14/5/310)

INSTITUTE OF PHYSICS PUBLISHING JOURNAL OF PHYSICS: CONDENSED MATTER

J. Phys.: Condens. Matter **14** (2002) 1061–1065 PII: S0953-8984(02)28929-8

Modulated magnetic ordering in the Cu-doped pseudoperovskite system $CaCu_xMn_{3-x}Mn_4O_{12}$

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Received 12 August 2001, in final form 19 September 2001
Published 25 January 2002
Online at stacks.iop.org/JPhysCM/14/1061

Abstract

The crystal and magnetic structures of the $CaCu_xMn_{3-x}Mn_4O_{12}$ compounds with $x = 0.3$ and 0.7 were investigated by means of x-ray and neutron powder diffraction. The crystal structure parameters of the $x = 0.3$ compound at 60 K have been refined within the trigonal space group $R\bar{3}$. The magnetic moments of Mn ions in the $x = 0.3$ sample become ordered below 40 K. The magnetic ordering is modulated with a propagation vector $(0, 0, \kappa)$. A model of the magnetic structure which is in agreement with the experimental data is proposed along with an estimation of the temperature dependence of the magnetic moment value. The magnetic ordering has a reduced correlation length of about 250 Å. The $x = 0.7$ compound does not show any long-range magnetic ordering down to 1.5 K.

1. Introduction

The various physical properties of several manganese perovskite materials have recently been under very active investigation because of the interesting interplay between their magnetic, electronic and structural properties [1–3]. Most of these phenomena are related to magnetic, charge, and orbital orderings of interpenetrating sublattices of Mn^{3+} and Mn^{4+} ions in the material. The interesting magnetic phase transitions observed in $CaMn_7O_{12}$ [4–6] as well as recent macroscopic studies of colossal magnetoresistivity (CMR) performed on Cu-doped $CaCu_xMn_{3-x}Mn_4O_{12}$ [7] motivated us to study the magnetic ordering in these Cu-doped compounds.

In this paper we present the results of neutron and x-ray diffraction studies of the Cu-doped distorted perovskite-type manganites $CaCu_xMn_{3-x}Mn_4O_{12}$ with two compositions, $x = 0.3$ and 0.7. Studies by Bochu *et al* [8] have shown that the undoped compound $CaMn_7O_{12}$ has a trigonal structure at RT (space group $R\bar{3}$). The structure of the fully Cu-doped compound $CaCu_3Mn_4O_{12}$ (i.e. $x = 3$) is cubic at RT (space group $Im\bar{3}$) as reported by Chenavas *et al* [9]. According to Troyanchuk and Chobot [10], this family of compounds has a high-temperature

Table 1. Structural parameters of $CaCu_{0.3}Mn_{6.7}O_{12}$ obtained from Rietveld refinement of the neutron diffraction pattern measured at 60 K. The space group is trigonal $R\bar{3}$ and the lattice constants in the hexagonal setting are $a_h = 10.4015(12)$ Å and $c_h = 6.3636(15)$ Å. One overall isotropic temperature factor was used: $B = 0.72(2)$ Å^2. The conventional Rietveld reliability factors are $R_p = 10.5\%$, $R_{wp} = 9.77\%$, $R_{\text{exp}} = 5.1\%$, $\chi^2 = 3.7\%$, and $R_{\text{Bragg}} = 3.5\%$.

Atom	Position	x	y	z	Occupancy
Ca	(3a)	0	0	0	1.0
Mn	(9e)	1/2	0	0	0.892(6)
Cu	(9e)	1/2	0	0	0.108(6)
Mn	(9d)	1/2	0	1/2	1.00
Mn	(3b)	0	0	1/2	1.00
O	(18f)	0.2237(19)	0.2700(16)	0.0841(31)	1.00
O	(18f)	0.3456(26)	0.5221(26)	0.3421(23)	1.00

cubic phase and a low-temperature trigonal phase. The transition temperature decreases with increasing Cu content—x. For $CaMn_7O_{12}$ ($x = 0$) it is 440 K while for $CaCu_{0.3}Mn_{6.7}O_{12}$ ($x = 0.3$) it is 310 K. For $x \geqslant 0.4$ it was suggested that a possible cubic-to-trigonal phase transition takes place below 100 K [10].

2. Crystal structure

The x-ray powder diffraction measurements were performed at RT with a standard laboratory Cu Kα x-ray diffractometer. The neutron powder diffraction measurements were performed at several temperatures between 60 and 1.5 K by using the diffractometer E2 at the Berlin Neutron Scattering Centre. The x-ray diffraction measurements performed at RT for the two $CaCu_xMn_{3-x}Mn_4O_{12}$ samples are in agreement with the proposed cubic crystal structure described, with the space group $Im\bar{3}$. Neutron powder diffraction measurements on the $x = 0.3$ sample were performed at $T = 60$ K with a neutron wavelength of $\lambda = 1.221$ Å in the angular range $5.0° \leqslant 2\theta \leqslant 102.0°$. The observed neutron powder diffraction pattern was analysed by the Rietveld method by using the program FullProf [11] and the trigonal model of the structure (space group $R\bar{3}$ in the hexagonal setting). The following atomic positions were assumed [8]: Ca ions in (3a) positions; Mn in (9d) and (3b) positions; Mn ions mixed with Cu ions in (9e) positions; and finally O ions in two different (18f) positions. The analysed diffraction pattern contained several peaks which could not be indexed with the $CaCu_xMn_{3-x}Mn_4O_{12}$ structure. These peaks were identified as to be due to the Mn_3O_4 impurity phase [12, 13] which was also incorporated in the refinement. The resulting structural parameters of $CaCu_{0.3}Mn_{6.7}O_{12}$ are given in table 1. The relative volume content of the Mn_3O_4 impurity was estimated as 3%. The refined occupancy of Cu ions gives an estimate of $x = 0.324(16)$, showing good agreement with the assumed value of $x = 0.3$. One should note that due to resolution limitations it was impossible to observe splittings of powder diffraction peaks due to trigonal symmetry and that the data could also be satisfactorily refined with a cubic crystal structure model. The powder neutron diffraction pattern of $CaCu_{0.7}Mn_{6.3}O_{12}$ measured at 20 K with the neutron wavelength 2.41 Å agrees with the cubic crystal structure described with the space group $Im\bar{3}$, but we are unable to decide whether the structure is trigonal or not.

3. Magnetic ordering

Neutron powder diffraction measurements on $CaCu_xMn_{3-x}Mn_4O_{12}$ have been performed between 60 and 1.5 K by using the neutron wavelength $\lambda = 2.41$ Å. The nuclear diffraction

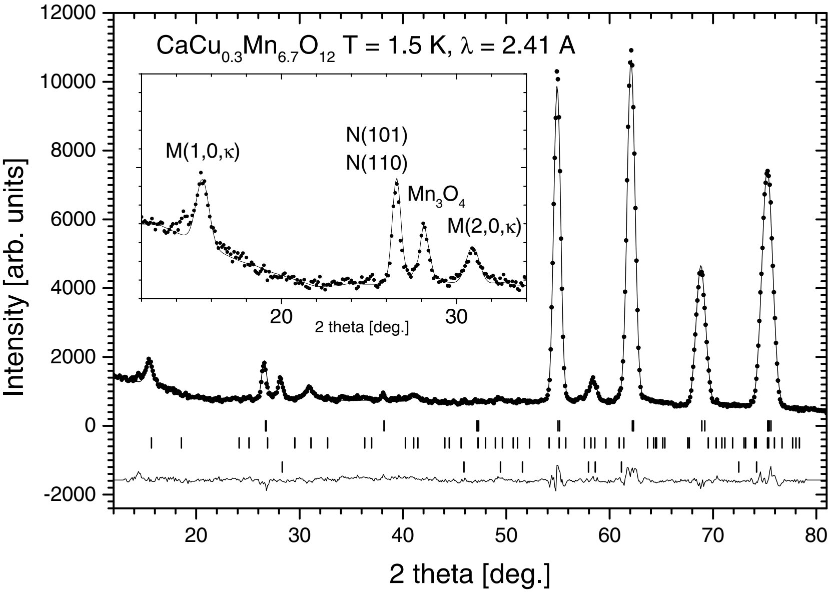

Figure 1. Results of the Rietveld refinement of the powder neutron diffraction pattern of $CaCu_{0.3}Mn_{6.7}O_{12}$ measured at 1.5 K. The measured data (solid circles) are shown together with the resulting fit (continuous curve) and their difference plot (the continuous curve below). The ticks show the predicted 2θ positions for the nuclear peaks of $CaCu_{0.3}Mn_{6.7}O_{12}$ (upper row), the magnetic peaks of $CaCu_{0.3}Mn_{6.7}O_{12}$ (middle row), and the nuclear and magnetic peaks of the Mn_3O_4 impurity (lower row). The inset shows the enlarged low-angle part of the same diffraction pattern. One can see the magnetic (110) reflection due to Mn_3O_4.

peaks can be described by using the trigonal structural model described above. The low-temperature neutron diffraction patterns of $CaCu_{0.3}Mn_{6.7}O_{12}$ contain several magnetic diffraction peaks which vanish between 40 and 45 K. One should note that this is in disagreement with the findings of Troyanchuk *et al* [14], who reported the absence of any long-range magnetic ordering in $CaCu_{0.4}Mn_{6.6}O_{12}$ at 4.2 K.

First of all, it was found that the magnetic peak near $2\theta = 28.2^\circ$ is the strongest magnetic reflection (101) of Mn_3O_4 [12, 13]. The other magnetic diffraction peaks of Mn_3O_4 are much weaker than the (101) peak and they were not detected in our measurements. A model of the magnetic ordering already observed in $CaMn_7O_{12}$ [5] has been taken into account. The Mn ions located in the (9d), (9e) and (3b) sublattices are arranged in horizontal planes. The Mn ions lying in the same horizontal plane and the same sublattice have parallel magnetic moments. We have assumed the following magnetic moment directions: for (9d): $z = 1/6 \downarrow$, $z = 3/6 \uparrow$, $z = 5/6 \downarrow$; for (9e) $z = 0/6 \uparrow$, $z = 2/6 \downarrow$, $z = 4/6 \downarrow$; and for (3b) $z = 1/6 \uparrow$, $z = 3/6 \downarrow$, $z = 5/6 \uparrow$ (where $\uparrow$ and $\downarrow$ mean parallel and antiparallel to a given direction). The magnetic peaks observed in $CaCu_{0.3}Mn_{6.7}O_{12}$ lie at 2θ angles larger than the commensurate $(1, 0, 0)$, $(2, 0, 0)$, $\ldots$, etc peak positions, but they can be indexed as $(1, 0, \kappa)$, $(2, 0, \kappa)$. Taking into account the similar magnetic ordering observed in $CaMn_7O_{12}$ [5], it was assumed that the basic ferrimagnetic ordering described above is modulated with a propagation vector $(0, 0, \kappa)$. The magnetic moments form a helix and they are confined to the (a, c) plane. The resulting Rietveld refinement of the neutron powder diffraction pattern observed at 1.5 K with that helical model of the magnetic ordering is shown in figure 1. The same model of magnetic ordering agrees also with the diffraction patterns measured at other temperatures up to 40 K. The refined

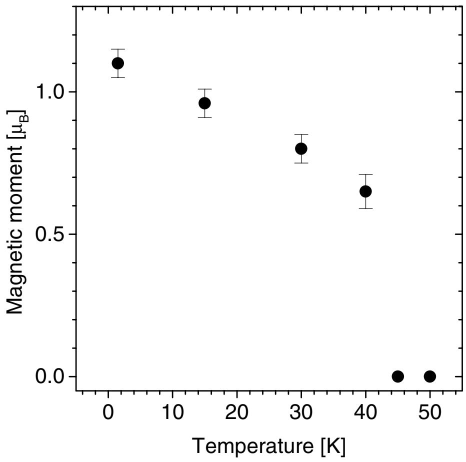

Figure 2. The temperature dependence of the values of the magnetic moments of Mn ions in $CaCu_{0.3}Mn_{6.7}O_{12}$ obtained from Rietveld analysis of the neutron diffraction data (see the text).

value of the propagation vector length $\kappa = 0.145(10)c^*$ corresponds to a modulation period of 43(3) Å and it does not change with temperature. The values of the magnetic moments of Mn ions in all three crystallographic sublattices were kept equal during the refinement. The temperature dependence of the refined values of the magnetic moments of Mn ions is shown in figure 2. The values of the magnetic moments of Mn ions in different sublattices can, in principle, be different because of the Cu content in sublattice (9e) and also because most probably the Mn^{4+} ions occupy preferentially the (3b) sublattice, as in $CaMn_7O_{12}$ [8]. Refinements with different values of the magnetic moments of Mn ions in different sublattices were also performed. The improvement of the fit quality was not significant and the statistical errors of the magnetic moment values were larger than in the refinement with all magnetic moments equal. Another important feature of the magnetic diffraction peaks observed for $CaCu_{0.3}Mn_{6.7}O_{12}$ is that they are broader than the neighbouring nuclear peaks. From the broadening, one can estimate that the magnetic correlation length ξ in $CaCu_{0.3}Mn_{6.7}O_{12}$ is about 250(50) Å and it does not change with temperature. Such a limited magnetic correlation length was also observed in $CaMn_7O_{12}$ near the magnetic phase transition at 49 K.

The neutron powder diffraction pattern of $CaCu_{0.7}Mn_{6.3}O_{12}$ measured at 1.5 K does not show any magnetic peaks, so we can conclude that there is no long-range magnetic ordering in this compound, in agreement with [14].

Acknowledgments

Thanks are due to Dr I O Troyanchuk for providing us with the samples. This work was partially supported by the Committee for Scientific Research (Poland). The measurements performed at BENSC were supported by the European Commission under the Access to Research Infrastructures Action of the Human Potential Programme (contract HPRI-CT-1999-00020).

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