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Metamagnetic transition of martensitic type in electron-doped manganites $Ca_{1-x}Ce_xMnO_3$ (x = 0.10, 0.12)

N.N. Loshkareva [a,*], D.I. Gorbunov [a,b,c], A.V. Andreev [b], N.V. Mushnikov [a], Y. Skourski [d], F. Wolff-Fabris [d,1]

[a] Institute of Metal Physics UB RAS, Kovalevskaya 18, 620990 Ekaterinburg, Russia
[b] Institute of Physics, Academy of Sciences, Na Slovance 2, 182 21 Prague, Czech Republic
[c] Department of Condensed Matter Physics, Charles University, Ke Karlovu 5, 121 16 Prague, Czech Republic
[d] Dresden High Magnetic Field Laboratory, Helmholtz-Zentrum Dresden-Rossendorf, 01314 Dresden, Germany

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ABSTRACT

Magnetic and electrical properties of electron-doped manganites $Ca_{0.88}Ce_{0.12}MnO_3$ and $Ca_{0.90}Ce_{0.10}MnO_3$ were studied in pulsed magnetic fields up to 60 T in the temperature range T = 1.5–260 K. Metamagnetic transition caused by the melting of the charge/orbital ordering and martensitic structural transition in a magnetic field was revealed. The transition is accompanied by a change in electrical resistivity of the sample by three orders. A magnetic phase diagram in the plane of the H–T was constructed. Higher values of the critical transition fields for the system $Ca_{1-x}Ce_xMnO_3$, compared to the known system $Ca_{1-x}Sm_xMnO_3$ are explained by a narrower range of phase separation and a bigger difference between the Néel temperatures of the C and G-type antiferromagnetic phases, which originated from the difference between the valence of the Ce^{4+} and Sm^{3+} ions.

1. Introduction

In recent years much attention has been devoted to manganites of the $A_{1-x}Ln_xMnO_3$ (A – alkaline earth ions Ca, Sr; Ln – rare-earth ions or their combinations) type, in which large-scale phase separation is present, i.e., the co-existence of well-defined crystallographic and magnetic phases and phases with different conductivity, charge and orbital ordering. Giant magnetoresistance and other effects related to competition of the co-existent phases have been found in this type of manganites [1,2]. For manganites with different Ca concentrations (with hole doping of $La_{0.275}Pr_{0.35}Ca_{0.375}MnO_3$, electron doping of $Bi_{0.2}Ca_{0.8}MnO_3$ and half-doping of $Pr_{1/2}Ca_{1/2}MnO_3$), evidence supporting martensitic nature of the charge-ordered (CO) phase has been obtained in studies of electrical resistivity in a magnetic field and morphology of the CO phase by polarizing optical spectroscopy [3]. The martensitic phase is characterized by growth of CO regions of a lenticular shape, rapid propagation of the boundaries of structural domains through the crystal upon martensite formation, thermal hysteresis of electrical resistivity at the charge ordering temperature T_{CO} [3].

Unusual staircase-like metamagnetic transitions have been observed in ceramic manganite samples $Pr_{0.5}Ca_{0.5}Mn_{0.97}Ga_{0.03}O_3$ in magnetic fields up to 9 T at T = 2.5 K [4]. The strong influence of annealing and grinding on the staircase-like structure of magnetization of the manganites was attributed in Ref. [4] to martensitic nature of the metamagnetic transitions.

The $Ca^{2+}_{1-x}Ce^{4+}_xMnO_3$ (x = 0.10, 0.12) compounds studied in the present work belong to electron-doped manganites of the $Ca_{1-x}Ln_xMnO_3$ type with tri- or tetravalent rare-earth ions Ln within the $0 \leqslant x \leqslant 0.20$ concentration range, where different crystal and magnetic structures have been observed [5–9]. The formal valence of cerium (4+) was found for $Ca_{1-x}Ce_xMnO_3$ ($0 \leqslant x \leqslant 0.20$) system using the X-ray absorption spectroscopy [10]. Thus, substitution of Ca^{2+} ion by Ce^{4+} ion produces a two-electron doping of $CaMnO_3$. Manganite $CaMnO_3$ crystallizes in the orthorhombic *Pnma* structure and has antiferromagnetic (AFM) ordering of the G-type in which the spin of each Mn^{4+} ion is antiparallel to the spins of six nearest neighbor Mn^{4+} ions; doping of $CaMnO_3$ with Ln ions results in the appearance of ferromagnetic (FM) clusters and/or a canted magnetic structure with a FM component in the AFM phase of the G-type. The crystal structure of $Ca_{0.8}Ln_{0.2}MnO_3$ is monoclinic (of the $P2_1/m$ space group) with charge/orbital ordering and AFM ordering of the C-type (without FM contribution) which is characterized by a ferromagnetic ordering of the magnetic moments of Mn ions in chains and by an antiferromagnetic ordering between neighboring chains. For this reason the doping first leads to an

* Corresponding author. Tel.: +7 343 3783810; fax: +7 343 3745244.
E-mail address: loshkareva@imp.uran.ru (N.N. Loshkareva).
[1] Present address: European X-ray Free-Electron Laser Facility GmbH, Notkestrasse 85, 22607 Hamburg, Germany.

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increase and then a decrease in low-temperature magnetization and conductivity [5,6]. One of the interesting and unusual phenomena that occur on the boundary of the AFM phases of the *G* and *C*-type is melting of the charge/orbital ordering in a strong magnetic field [11]. Magnetization curves of electron-doped manganites $Ca_{1-x}Sm_xMnO_3$ with Sm concentration $x = 0.14$ and 0.15 at $T = 4.2$ K are of metamagnetic character with hysteresis $\mu_0H \sim 10$ T at the critical fields of the transition. The highest value of the magnetic moment in a field of 30 T for both samples was $\sim 2\ \mu_B$/Mn, which is lower than the theoretical value at saturation. The neutron diffraction data for the composition with $x = 0.15$ at low temperatures reported in [11] indicated the co-existence of two crystal ($P2_1/m$ and *Pnma*) and two magnetic phases (*C* and *G*-type), i.e., large-scale phase separation. As shown in Ref. [12], application of a magnetic field of $\mu_0H = 7$ T reduced electrical resistivity of $Ca_{0.85}Sm_{0.15}MnO_3$ by four orders of magnitude at $T = 4.2$ K.

When studying magnetization curves of single crystals of electron-doped manganites $Ca_{1-x}Ce_xMnO_3$ ($x \leqslant 0.12$) in pulsed magnetic fields up to $\mu_0H = 35$ T, we found a metamagnetic transition for the Ce concentration $x = 0.10$ and 0.12 in the temperature range 77–240 K [13,14]. However, at $T = 4.2$ K no metamagnetism was observed. According to the estimation made in Ref. [14], the critical fields at low temperatures can be as high as 50–60 T for these manganites. The reason for such high expected critical magnetic fields for the manganite $CaMnO_3$ doped with Ce in comparison with the critical magnetic field $\mu_0H_c \sim 10$ T for the manganite doped with Sm with $x = 0.14$ and 0.15, is not yet clear. Since the magnetic subsystem of the manganites is strongly connected with the electronic subsystem, it is necessary to study electrical resistivity in the fields where the metamagnetic transition is observed. In order to elucidate the nature of the interactions among the electronic, magnetic and lattice subsystems in the strongly correlated compounds with charge/orbital ordering, in this work magnetization and electrical resistivity of the $Ca_{1-x}Ce_xMnO_3$ manganites are studied in pulsed magnetic fields up to 60 T.

2. Experimental details

$Ca_{1-x}Ce_xMnO_3$ ($x = 0.10$, 0.12) single crystals were grown by the floating zone method with radiation (light) heating at a rate of 8.5 mm/h in air flow on an URN-2-ZP setup in Moscow Power Engineering Institute [15]. An X-ray diffraction study showed that in the single crystals with $x = 0.10$ and 0.12 at room temperature, apart from the pseudocubic lattice (with orthorhombic distortions), the monoclinic $P2_1/m$ phase is present with a dominant volume fraction for the composition with $x = 0.12$. The lattice parameters of the monoclinic phase for the composition with $x = 0.10$ are $a = 5.326$ Å, $b = 7.502$ Å, $c = 5.300$ Å, $\beta = 90.10°$; for the composition with $x = 0.12$, $a = 5.336$ Å, $b = 7.509$ Å, $c = 5.310$ Å, $\beta = 90.26°$, the parameter of the pseudocubic lattice is $2a_c = 7.503$ Å. As noted in Ref. [15], the $Ca_{1-x}Ce_xMnO_3$ ($0 < x \leqslant 0.12$) single crystals grown by the floating zone method contained a considerable amount of cation vacancies predominant over oxygen vacancies in comparison with polycrystals studied earlier in [5]. On account of the complicated phase composition and the presence of twins and defects, measurements of anisotropy of physical properties cannot be done on these samples.

Temperature dependencies of electrical resistivity and magnetization under steady magnetic fields were measured using a Physical Properties Measurement System (Quantum Design) in the temperature range $T = 2$–300 K. The high-field magnetization curves were measured in pulsed magnetic fields up to 60 T with a total pulse duration of 25 ms (magnet KS21c) using the magnetometer installed in the Dresden High Magnetic Field Laboratory. In order to reduce the influence of the magnetic anisotropy and eddy currents on the shape of the magnetization curves, the samples for the magnetic measurements were manually ground in an agate mortar into a powder with a particle size ~80 μm.

Electrical resistivity for the composition with $x = 0.12$ was measured on a bulk sample in pulsed magnetic fields up to 63 T (magnet KS3rc with pulse duration of 150 ms). The experiments were carried out with a He-4 flow cryostat for measurements at temperatures from $T = 1.5$ K up to $T = 300$ K. The sample used in these experiments had dimensions $3.8 \times 1.9 \times 1.3$ mm^3 and we performed the measurements using a standard 4-contacts technique with AC current of 1 mA and 13 kHz. The applied current and the obtained voltage of the sample are measured simultaneously as function of time during the total pulse duration using a fast acquisition system DL750 Yokogawa Oscilloscope equipped with a 16-bits and 1 M sample/s digitizing cards. The measured data are processed with a digital lock-in program in order to calculate the magnetoresistance curves as function of applied magnetic field.

3. Results and discussion

Magnetic and electrical properties of the $Ca_{1-x}Ce_xMnO_3$ ($x \leqslant 0.12$) single crystals in magnetic fields up to 9 T have been studied before in Ref. [15]. The results were interpreted using the neutron diffraction and high-resolution synchrotron X-ray diffraction data obtained in Ref. [16] for stoichiometric $Ca_{1-x}Ce_xMnO_3$ polycrystals. The polycrystals with cerium concentration $0.1 \leqslant x \leqslant 0.1$ 67 studied in Ref. [16] also had the monoclinic $P2_1/m$ structure at room temperature. With decreasing temperature a charge-ordered state of the Wigner crystal type and *C*-type AFM structure ($P_{2a}2_1/m$) were observed in them.

Temperature dependencies of electrical resistivity ρ and magnetization M in a magnetic field of $\mu_0H = 5$ T, presented in Fig. 1 (data from Ref. [15]), demonstrate the temperature evolution of the electronic and magnetic states of the $Ca_{1-x}Ce_xMnO_3$ ($x = 0.10$, 0.12) single crystals. Electrical resistivity of the samples displays semiconductor-like behavior in the whole temperature range. The temperature of the onset of the sharp $\rho(T)$ growth upon cooling coincides with the maximum in magnetization. The resistivity growth and magnetization drop are related to charge/orbital ordering. The ordering temperature $T_{CO/OO}$ for the crystal with $x = 0.10$ is 185 K and for the crystal with $x = 0.12$ it is equal to 222 K [15]. The temperature hysteresis of magnetization in the range $T =$100–300 K points to the first-order transition from the orthorhombic paramagnetic semiconducting phase to the monoclinic *C*-type antiferromagnetic charge-ordered isolating phase. The Néel temperature of the *C*-type AFM phase for the sample with $x = 0.12$ determined by the extremum of the dM/dT derivative is $T_N(C) = 153$ K, for $x = 0.10$ it is estimated to equal $T_N(C) = 155$ K.

Magnetization curves of $Ca_{0.88}Ce_{0.12}MnO_3$ and $Ca_{0.90}Ce_{0.10}MnO_3$ measured in pulsed magnetic fields up to 60 T at $T = 1.5$–180 K are shown in Fig. 2. It is seen that in this temperature and field range a metamagnetic transition is observed for both samples. The transition is accompanied by a substantial field hysteresis characteristic of first-order phase transitions. Magnetization curves of the samples at temperatures above $T = 150$ K coincide with those of the same samples measured earlier in pulsed fields up to 35 T [13,14].

At lower temperatures a considerable difference in the shape of the magnetization curves is observed since a magnetic field of 35 T is not sufficient to complete the metamagnetic transition. For the compositions with $x = 0.10$ and 0.12 at temperatures 120 and 160 K, respectively, in fields up to 35 T the maximal values of the

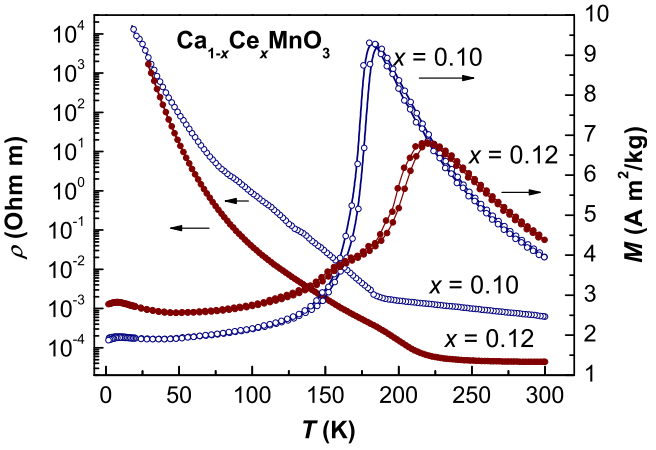

Fig. 1. Temperature dependences of magnetization in a magnetic field 5 T and electrical resistivity for $Ca_{1-x}Ce_xMnO_3$ single crystal with $x = 0.10$, and 0.12.