Pis'ma v ZhETF, vol.70, iss.9, pp.583 - 587

EFFECT OF OXYGEN CONTENT ON MAGNETIC STATE OF THE $La_{0.5}Ca_{0.5}MnO_{3-\gamma}$ PEROVSKITES

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Submitted 21 September 1999

The magnetization and magnetoresistance were studied in $La_{0.5}Ca_{0.5}MnO_{3-\gamma}$ as a function of oxygen content. It is found that upon reduction of oxygen content this compound undergoes a sequence of transitions from antiferromagnetic into ferromagnetic state ($\gamma \geq 0.04$), from ferromagnetic into spin-glass state ($\gamma \geq 0.14$) and spin-glass transforms into inhomogenious ferromagnetic state ($\gamma \geq 0.25$). Strongly reduced samples ($\gamma \geq 0.25$) show a large magnetoresistance despite the absence of Mn^{3+}-Mn^{4+} pairs. It is suggested that oxygen vacancies in the samples reduced strongly ($\gamma \geq 0.25$) are long range ordered.

PACS: 72.15.Gd, 75.30 Kz, 75.50.Lk

The issue of charge ordering in $Ln_{0.5}A_{0.5}MnO_3$ (Ln=lanthanide, A – alkaline earth element) manganites has attracted considerable attention during the last few years after discovery of CMR effect associated with charge order-disorder transition [1]. In fact this phenomenon was studied for the first time in $La_{0.5}Ca_{0.5}MnO_3$ by Wollan and Koehler [2] and by Goodenough [3]. The $La_{0.5}Ca_{0.5}MnO_3$ compound undergoes first a ferromagnetic transition at 260 K and then a simultaneous antiferromagnetic and charge ordering transition at a lower temperature. The magnetic arrangement associated with 1:1 Mn^{3+}/Mn^{4+} order consists of stacked antiferromagnetic octants C and E. The low temperature crystal structure has been shown to be incommensurate [4, 5].

It is well known that magnetic ground state of $LaMnO_{3-\gamma}$ parent compound depends on oxygen content [6]. This compound shows a concentrational antiferromagnet-ferromagnet transition as oxygen content increases. In contrary the $La_{0.6}Ba_{0.4}MnO_3$ compound shows collaps of long range ferromagnetic arrangement as oxygen content decreases [7]. However to our knowledge, the magnetic and transport properties of charge ordered $Ln_{0.5}A_{0.5}MnO_3$ (Ln=lanthanide) manganites in dependence on oxygen content are unknown to date. In this report we present a detailed study of the variation of magnetic state with oxygen content for the $La_{0.5}Ca_{0.5}MnO_{3-\gamma}$ manganites.

The $La_{0.5}Ca_{0.5}MnO_3$ compound was prepared by standard solid state reaction at $T = 1500\,^{\circ}C$ in air. After synthesis the sample was annealed at 900 °C for 100 h in air in order to receive the oxygen saturated compound. The annealed sample was cut into pieces and reduced in silica tubes at 900 °C using metallic thantalum as an oxygen getter. After reduction the change of weight was measured. The starting material $La_{0.5}$ $Ca_{0.5}MnO_3$ is found to be stoichiometric in agreement with thermogravimetric study at 1000 °C in the flowing hydrogen. The oxygen content of reduced samples was determined from the weight change during reduction. The phase characterization and determination of lattice parameters were performed with powder X-ray diffraction analysis. Electrical resistivity

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was measured by the dc four probe method and the magnetization was determined using Foner vibrating sample magnetometer.

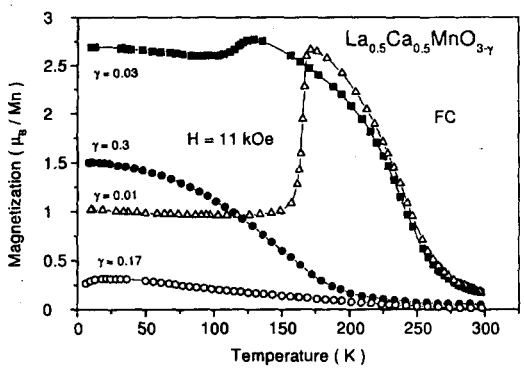

Fig.1.Magnetization of the $La_{0.5}Ca_{0.5}MnO_{3-\gamma}$ samples as a function of temperature

The $M(T)$ and $M(H)$ curves for the $La_{0.5}Ca_{0.5}MnO_{3-\gamma}$ phases are displayed in Fig.1 and Fig.2 respectively. The stoichiometric compound exhibits enhancement and drop of magnetization on warming at 180 and 260 K respectively. In agreement with literature data anomalous behavior around 180 K is associated with antiferromagnet-ferromagnet transition whereas at 260 K there is the Curie point. The anomaly due to antiferromagnet-ferromagnet transition is much less pronounced for the oxygen deficit phase with γ=0.03 (Fig.1). This phase shows the Curie point 260 K and magnetic moment 3.3 μ_B per $(Mn^{3+}_{0.5}Mn^{4+}_{0.5})$ unit at 6 K, i.e. slightly smaller than the expected value calculated from pure ionic model (3.5 μ_B). The magnetic behavior of the phases in the oxygen range $0.14 \leq \gamma \leq 0.2$ is incompatible with ferromagnetic behavior because their magnetic moments are much less than those expected for ferromagnetic ordering (Figs.1, 2). Both a strong magnetization dependence on magnetic field and broad transition into magnetically disordered state are consistent with inhomogenous low temperature magnetic state. Surprisingly the magnetization increases strongly while the content of oxygen vacancies becomes close to γ=0.25 i.e., all manganese ions adopt three valent state (Figs.1, 2). However, magnetic moment at 6 K is only 1.5 μ_B per manganese ions whereas for ferromagnetically ordered phase expected value is around 4 μ_B. Further insight into magnetic state of oxygen deficit phases is gained from zero field cooled (ZFC) and field cooled (FC) magnetization recorded in a relatively small (100 Oe) magnetic field (Fig.3). For γ=0.17 phase we have first observed fast increase of ZFC magnetization up to 50 K, then ZFC magnetization depends slightly on temperature and, finally decreasing magnetization in the range 160–200 K indicates a transition into paramagnetic state. By contrast the FC magnetization demonstrates very weak temperature dependence in the low temperature range (5-50 K) (Fig.3) whereas above 50 K FC magnetization decreases gradually with increasing temperature. Take into account magnetic data recorded in a charge magnetic field one can conclude that such a behavior of ZFC and FC magnetizations could result from large magnetic clusters of magnetic moments being gradually blocking with decreasing temperature. Below 50 K magnetic anisotropy increases strongly apparently due to magnetic frustration.

The drop magnetization associated with transition into paramagnetic state becomes more pronounced for $La_{0.5}Ca_{0.5}MnO_{2.75}$. This compound undergoes the transition into magnetically ordered state slightly below 200 K. A difference between ZFC and FC magne-

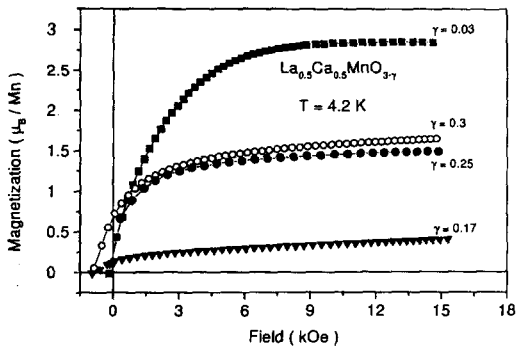

Fig.2. Magnetization of the $La_{0.5}Ca_{0.5}MnO_{3-\gamma}$ samples as a function of magnetic field

tizations is smaller than that for γ=0.17 compound whereas ZFC magnetization does not change below 50 K thus indicating a decrease of antiferromagnetic component. Further increase of oxygen vacancies up to γ=0.3 does not change sufficiently magnetic properties.

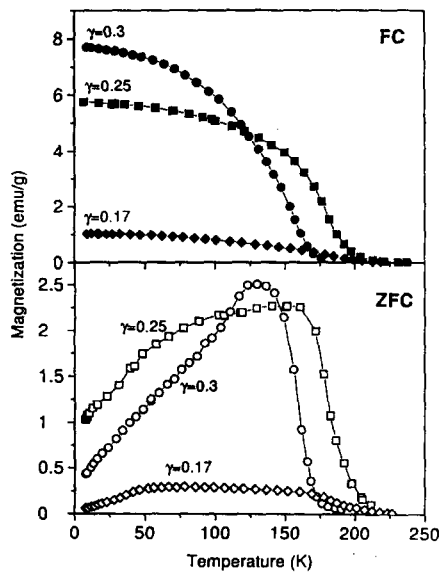

Fig.3. ZFC and FC magnetizations of $La_{0.5}Ca_{0.5}MnO_{3-\gamma}$ as a function of temperature

All oxygen deficit compounds ($\gamma \geq 0.04$) show semiconductive behavior below Curie point. Magnetoresistance strongly decreases while concentrational transition from long-range to short-range magnetic order occurs. The resistivity and magnetoresistance for γ=0.25 are shown in Fig.4. This compound demonstrate insulating behavior in the whole studied temperature interval. Below Curie point the magnetoresistance increases strongly, however, there is no peak of the magnetoresistance around Curie point as it was observed for oxidized manganites.

The electrical conductivity and ferromagnetism in the manganites were explained in terms of the double exchange interaction with transfer of electron from Mn^{3+} to Mn^{4+} ions [8, 9]. The effect of an applied field is to favour this electron transfer by reducing spin disorders leading to a negative magnetoresistance. However, in frame of this model impossible to understand ferromagnetic properties of the manganites without Mn^{4+} ions [10–12].

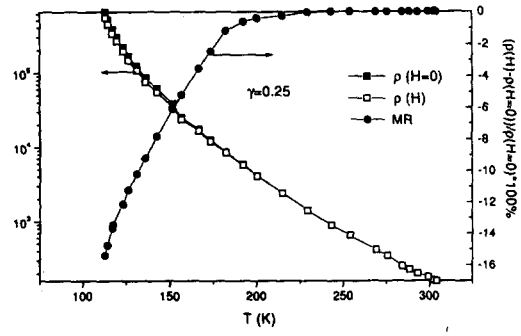

Fig.4. Resistivity and magnetoresistance of the $La_{0.5}Ca_{0.5}MnO_{2.75}$ sample as a function of temperature

Goodenough [12] adduced arguments for the ferromagnetism in the manganite to be due not only to double exchange but also to the specific character of the exchange interactions in the Jahn – Teller Mn^{3+} ion sistem. He proposed that the orbital configuration of the 3D electrons while removing the static Jahn – Teller distortions is determined by the ions nuclei position. In this case the dynamic enhancement of the ferromagnetic part of exchange interactions at the expense of correlation in the orbital orientation of neighbouring ions is to occur.

Leading a such consideration, ferromagnetic properties of $BiMnO_3$ and $LaMn_{1-x}Ga_xO_3$ where static Jahn – Teller distortions are removed could be explained. It is well known that the charge ordering in the manganites favors antiferromagnetic properties [3, 12]. However, from our data, the increase of the oxygen vacancies content ($\gamma \geq 0.04$) in $La_{0.5}Ca_{0.5}MnO_{3-\gamma}$ leads to a collapse of the ferromagnetic state in spite of the charge order disappearance. In our opinion this fact could be attributed to the strong negative superexchange interaction between manganese surrounded by oxygen vacancies and manganese occupying oxygen octahedra. At the relatively high oxygen vacancies concentration the antiferromagnetic exchange interaction dominates due to the strong negative (Mn^{3+}, coordination number five) – O^{2-} – (Mn^{3+}, coordination number six) superexchange interaction. This assumption is in agreement with antiferromagnetic properties of $CaMnO_{2.5}$ perovskite [13]. In order to explain the large ferromagnetic component of the strongly reduced $La_{0.5}Ca_{0.5}MnO_{3-\gamma}$($\gamma \geq 0.25$) we have suggested that the oxygen vacancies are distributed regularly over crystal lattice making up oxygen vacancies superstructure. In this case positive superexchange interactions between Mn^{3+} ions surrounded by six oxygen neighbors may be dominant thus leading to ferromagnetic properties of the strongly reduced manganites. From the literature data [14, 15] the perovskite-like manganites $LnBaMn_2O_{6-\gamma}$ (Ln=La,Y) with oxygen deficit ($\gamma \geq 0.5$) show oxygen vacancies ordering. However ferromagnetic component in $YBaMn_2O_{6-\gamma}$ is very weak [14]. Therefore we think that the crystal structures $LaCaMn_2O_{6-\gamma}$ and $LaBaMn_2O_{6-\gamma}$ are different. Further crystal and magnetic structure refinements are needed for better understanding magnetic properties of the calcium-doped manganites.

The authors acknowledge the financial support of Belarus fund for fundamental research under project F98-056 and NATO grant PST.CLG 975703.

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