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# Chemical effect on spin-electron subsystem of transition metal oxides

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Now one can say not only on the influence of spin subsystem on chemical properties , but also on possible chemical modification of spin subsystem. In this sense, the most effective way is controlled changing of the number of electrons by mild chemical reactions. Such physico-chemical modification is presented for somewhat different, chemically modified oxides of transition metal, namely, $YBa_2Cu_3O_7$, $LaMn_{1-x}(Ca/Sr)_xO_3$, $Ce_xSr_{1-x}MnO_3$, as initial compounds. The procedures of mild chemical treatment were described in [1,2].

i) $YBa_2Cu_3O_{7-x}$ . The experimental investigation of the changes induced by mild treatment by hydrogen at temperature near 420 K on the lattice parameters and $T_c$ of ceramic $YBCO_{7-x}$ were revealed their unusual behavior in comparison with the same for conventional oxygen-deficient samples. Chemically modified samples have showed $T_c \approx 85$ K even at x=0.35. This indicated that superconducting transition temperature is depended not only on the total oxygen content, but also on local ordering, first of all, reorientation of electron orbitals and then spin of apical oxygen. Our arguments and literature data will be discussed.

ii) $La_{067}(Ca/Sr)_{0.33}MnO_{3-a}$ solid solutions have been studied and compared. The physical characteristics of both series are accounted for as being due to a change in the $Mn^{3+}/Mn^{4+}$ ratio caused by oxygen removal. The differences between the strontium and calcium series originate from differences in both the bulk properties of the original oxygen-stoichiometric materials and their texture. In the strontium series, the texture manifests itself in intergrain magneto-resistance, which exceeds in magnitude the colossal magneto-resistance caused by bulk properties of the material. Study of the oxygen-deficient $La_{067}Sr_{0.33}Mn0_{3-a}$ compound revealed specific features in the dependence of the electro-physical parameters on temperature and the $Mn^{4+}$ fractional content that were not observed in the $La_{067}Ca_{0.33}Mn0_{3-a}$ studied by us and in $La_{1-x}Sr_xMn0_{3-a}$ samples described in the literature. The physics underlying these differences is discussed. A modified phase diagram relating the phase transition temperature to the $Mn^{4+}$ fraction was proposed.

iii) $Ce_xSr_{1-x}MnO_3$ .The electrical conductivity of $Ce_xSr_{1-x}MnO_3$ ($x$= 0.50, 0.67) prepared by skull-melting were studied in magnetic fields of up to 0.6 T in the temperature range 78–300 K. The semiconductor–metal phase transition is observed in ‘as prepared’ samples with x= 0.5 and in both annealed and ‘as prepared’ samples with $x$= 0.67. All samples exhibit GMR. The temperature dependence of the GMR, the dependence of the electrical resistivity on the magnetic field at 78 K, and the time dependence of the magnetoresistance at 78 K are measured for the first time. Some samples reveal the properties of spin glass and/or strong ferromagnetism. The reproducibility of the data obtained for these samples depends on the prehistory of the samples, specifically on the conditions of annealing and exposure to a magnetic field. The ‘competition’ of mixed-valent Ce and Mn for the state of electronic subsystem and their spines are discussed.

References

[1] Baikov Yu.M. Physics of the Solid State Vol.42, 6, 996, 2000
[2] Baikov Yu.M., Melekh B.T., Nikulin E.I., Physics of the Solid Stale, Vol. 49, 4, 696, 2000