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Studies of manganites by magnetic resonance spectroscopy methods

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ABSTRACT

In this work, we present the studies of manganites with superfluous manganese content performed by the magnetic resonance spectroscopy methods. The ferromagnetic resonance (FMR) has been measured on the $(\text{La}_{0.7}\text{Ca}_{0.3})_{1-x}\text{Mn}_{1+x}\text{O}_3$ films. The symmetrical FMR line in paramagnetic phase has the Dysonian-like shape below T_C . The FMR linewidth increases abruptly near the transition temperature. By comparing resonance fields oriented parallel and perpendicular to the film plane, the easy axis of magnetization was determined to be perpendicular to the film plane. In the perpendicular magnetic field, the spin-wave resonance (SWR) spectrum consisting of seventeenth of spin - wave modes has been observed in the $\text{La}_{0.7}\text{Mn}_{1.3}\text{O}_3$ film. Two of them observed on the high-field side of SWR spectrum are connected to a surface modes. The others are the bulk nonuniform spin-wave modes. Based on a study of temperature and angular dependencies of SWR and FMR spectra, the spin-wave stiffness, g-factor and exchange constant were established. An analysis of the ^{55}Mn NMR spectrum in $\text{La}_{0.6}\text{Sr}_{0.2}\text{Mn}_{1.2}\text{Cr}_{0.2}\text{O}_3$ has shown that a wide asymmetrical line can be uniquely expanded into four components with different resonance frequencies. There are manganese ions, which ionization states are close to (3^+) and (4^+) , as well as the Mn ions with intermediate valence resulted from the high-frequency electron exchange.

Keywords: resonance, FMR, NMR, spin-wave and surface modes, manganites, epitaxial films.

1. INTRODUCTION

In the last years, the investigations of monocrystal single-layer and multi-layer films of manganites with the general formula $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ demonstrating the effect of colossal magnetoresistance (CMR) is of an active interest. This is due to both their remarkable magnetic and transport properties and a potential application of the CMR effect¹.

The character of spin ordering at the transition to the ferromagnetic state was shown to influence on mobility of charge carriers and, correspondingly, on the electronic transport. Therefore, in studying of the magnetic properties of manganites, it is important to investigate the spin dynamics as it is intimately connected with charge motion between Mn^{3+} and Mn^{4+} ions. One of methods of spin dynamics study is ferromagnetic (FMR) and spin wave (SWR) resonance. The SWR spectrum can be excited in a ferromagnetic thin film if it exhibits appropriate boundary conditions. The pinning mechanism is responsible for excitation of the SWR spectra². If measurements of the bulk spin wave resonance in thin manganites films have been carried out, the observation of the surface spin-wave modes has not been reported yet.

In the $(\text{La}_{0.7}\text{Ca}_{0.3})_{1-x}\text{Mn}_{1+x}\text{O}_3$ compounds studied the cation deficiency responsible for the existence of mixed-valent $\text{Mn}^{3+} / \text{Mn}^{4+}$ ions is due to the provision of superfluous Mn content. The substitution La^{3+} with Mn induces the metal - insulator transition and the charge carriers due to this doping mediate the ferromagnetic interactions between the localized Mn spins³. The substitution of Mn with Cr ion is also of some interest because the Cr ion can exist in various ionization and magnetic states.

The main purpose of present paper to report the effect of superfluous manganese content on peculiarities of the FMR, SWR and NMR spectra in the manganites studied.

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2. SAMPLE PREPARATION AND CHARACTERIZATION

The FMR samples studied are the $(\text{La}_{0.7}\text{Ca}_{0.3})_{1-x}\text{Mn}_{1+x}\text{O}_3$ films epitaxially deposited onto the LaAlO_3 substrate using both DC-magnetron sputtering and pulsed-laser deposition. The DC sputtering of the $\text{La}_{0.7}\text{Mn}_{1.3}\text{O}_3$ films was realised in a 10 mTorr $\text{Ar}:\text{O}_2 = 4:1$ atmosphere. Temperature of the substrate surface was 600°C . In order to achieve a homogeneous films, the last were post-deposition annealed at 600°C for additional 30 min in oxygen flow. In the pulsed-laser deposition method, a 248 nm KrF excimer laser was used to deposit the films from stoichiometric targets. Deposition were carried out at oxygen pressure of 300 mTorr. The films were deposited on a substrate at temperature of 780 K. The films thickness measured by optical interferometry method was about 1000 - 3500 Å. According to the X-ray structural analysis, the films are single-phase and have perovskite structure with the lattice constant of 3.907 Å. The ceramic samples have been sintered using the standard technological method⁴. The obtained chemical composition for the $(\text{La}_{0.7}\text{Ca}_{0.3})_{1-x}\text{Mn}_{1+x}\text{O}_3$ compounds is assumed to conserve for films with an uncertainty of about 10 %.

The resonance measurements for in-plane and out-of plane magnetic field geometry were performed using a X-band reflection spectrometer operating at fixed frequency (about 9.235 GHz) in conjunction with a variable temperature flowing gas cryostat. Rotation of the sample was realized in the cavity in plane normal to the film plane with DC magnetic field changing its angle from the film normal to the film plane. The applied magnetic field was changed from 0 to 1.1 T. A HFF field was perpendicular to external magnetic field and was parallel to the film plane. Sample temperature was varied in steps from room temperature to liquid-helium temperature. The measurements of the ^{55}Mn NMR spectra determined using the two - pulse spin echo method have been carried out over a temperature of 77- 300 K.

3. EXPERIMENTAL RESULTS

3.1. Ferromagnetic resonance in the $(\text{La}_{0.7}\text{Ca}_{0.3})_{1-x}\text{Mn}_{1+x}\text{O}_3$ films

A typical FMR spectra for parallel and perpendicular to the film plane fields display one intensive peak identified

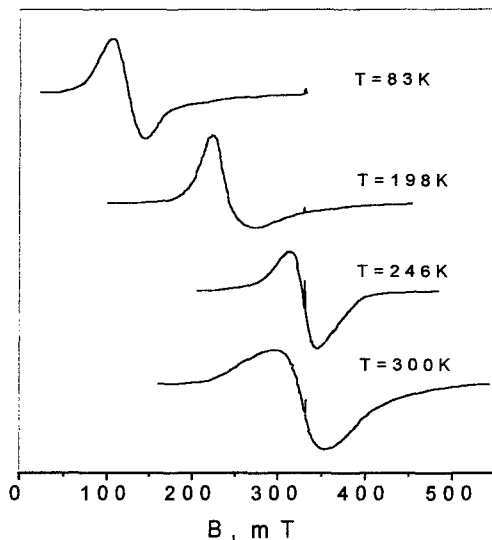


Fig.1 FMR spectrum in the parallel magnetic field geometry for different temperatures.

with the uniform procession FMR mode (Fig. 1). Almost symmetric FMR lines shape was observed in paramagnetic phase. Below T_C , the FMR signal shape becomes asymmetric (Dysonian-like) one. The resonance field H_{res} as a function of temperature for both the parallel (H_{\parallel}) and perpendicular (H_{\perp}) configurations of the applied magnetic field is well described by the equations for the resonance frequency: $\omega = \gamma (H_{\perp} - H_{\text{eff}})$ and $\omega = \gamma [H_{\parallel} (H_{\parallel} + H_{\text{eff}})]^{1/2}$, respectively, where $H_{\text{eff}} = 4\pi M_{\text{eff}} - 2H_A$. From experiment, we have $H_{\perp} > H_{\parallel}$. That is why in our case the anisotropy of easy-plane type is realized. It should be noted that the value of the effective magnetization $4\pi M_{\text{eff}}$ obtained from FMR is in satisfactory agreement with the SQUID data³. The anisotropy of H_{res} field was detected at $T < T_C$ when external field was scanned in the film plane. The anisotropy of linewidth was also fixed: ΔH_{pp} varies from 35 mT when $H \parallel [110]$ to 85 mT for $H \parallel [100]$.

The peak-to-peak linewidth increases sharply reaching the maximum value in the vicinity of T_C . A large peak in the linewidth near the transition temperature is a typical feature of manganite samples with magnetoresistive effect. One possible cause of such ΔH_{pp} behavior can be assumed to be an existence of AFM clusters near defects.

3.2. Spin-wave resonance in the $\text{La}_{0.7}\text{Mn}_{1.3}\text{O}_3$ films

According to the results of measurements for magnetic field perpendicular to the film plane, a resonance spectrum consists of eleven well-resolved lines (Fig. 2). Two of them on the high-field side we identify as the acoustic surface modes, SM_1 and SM_2 , while the others are the bulk nonuniform spin-wave modes. The following experimental facts give evidence for conclusion of surface character of SM_1 and SM_2 modes:

- (i) the resonance field of the modes is above the uniform-mode field position;
- (ii) the intensity of the modes is smaller than the next-lower field mode ($n = 1$);

(iii) the angle dependence of these modes is consistent with the predictions of surface-inhomogeneity model⁵.

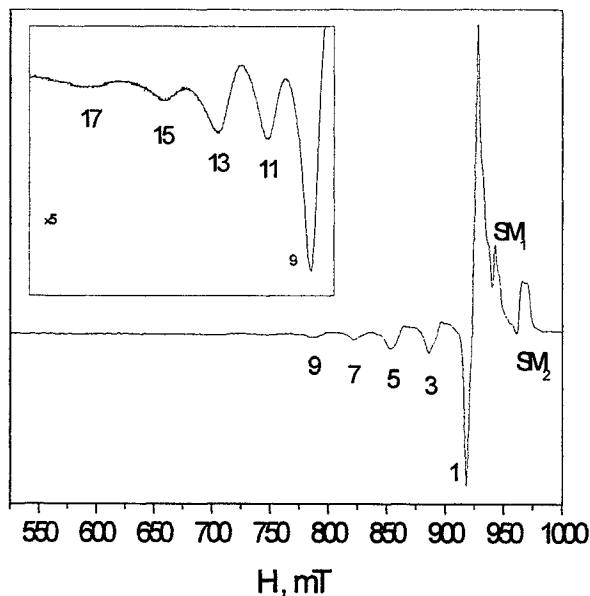


Fig.2 Spin-wave resonance spectrum in the perpendicular magnetic field at 100 K. The inset shows the higher number modes increased by a factor of five.

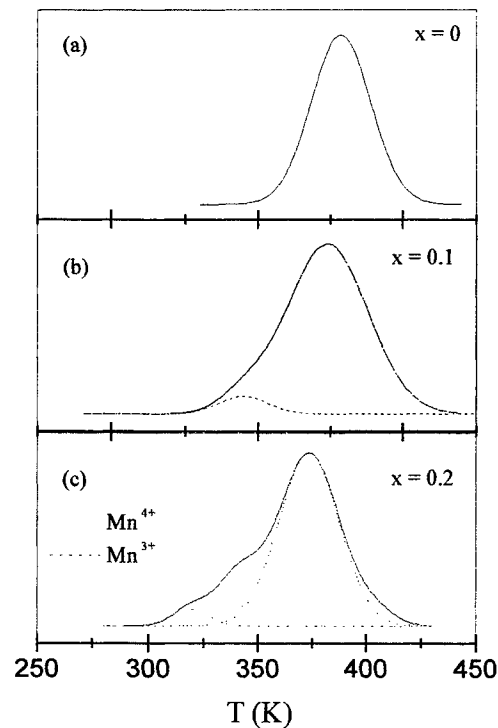


Fig.3 The ⁵⁵Mn NMR spectra in the La_{0.6}Sr_{0.2}Mn_{1.2-x}Cr_xO₃ compounds at 77 K.

Unusual transformation of the SWR spectrum is observed with decreasing temperature. Unlike nine lines of SWR observed below 165 K, the fifteenth and seventeenth modes occur only below $T = 143$ K and disappear at 48 and 87 K, respectively. Thus, the maximum number of detected modes is observed over a temperature range of 87 - 143 K.

Other interesting feature was detected in the temperature dependence of SWR linewidths. The linewidths of the higher-order modes ($n = 13, 15$ and 17) have nonmonotonic low temperature behaviour, namely, a decrease of $n=11$ mode linewidth is accompanied by occurrence of $n = 13$ mode. Similar behavior is observed for $n = 15$ mode.

According to an angular dependence of the mode positions, with deviation of field from perpendicular orientation, the resonance modes of SWR start to disappear. There exists a critical angle $\varphi_{cr} \approx 14^\circ$ between static magnetic field and the normal to the film ($90 \pm \varphi_{cr}$). For angles $\varphi < \varphi_{cr}$, a well-resolved multi-peaks SWR spectrum is detected, whereas for $\varphi > \varphi_{cr}$ the spectrum contains in general only one resonance absorption line. At critical angle, the surface and first spin-wave modes transform into the uniform mode. The uniform mode exists only in the region $0 < \varphi < \varphi_{cr}$.

Using the experimental data, we have made some quantitative estimations of the spin-wave stiffness constant, g -factor, saturation magnetization and exchange interaction parameter. Their values were obtained to be equal to $150 \text{ meV}\text{\AA}^2$, 1.96, 560 Oe and 32 K, respectively.

3.3. ⁵⁵Mn NMR in La_{0.6}Sr_{0.2}Mn_{1.2-x}Cr_xO₃ compounds

For the La_{0.6}Sr_{0.2}Mn_{1.2}O₃ sample ($x=0$), the NMR spectrum is a simple symmetric line (Fig. 3a) with the resonance frequency (379 MHz) intermediate between the frequencies characteristic for NMR lines of manganese ions in the trivalent state (400-430 MHz) and in the tetravalent state (319 MHz). The presence of one wide line in the spectrum indicates an electronic exchange between multivalent manganese ions with frequency considerably higher than the ⁵⁵Mn NMR frequency. It can be assumed that a surplus of Mn ions are in distorted A-sites in the divalent state. However, the NMR line in the region of 500-600 MHz typical of Mn²⁺ ions was not observed at 77 K. The ⁵⁵Mn NMR spectra in La_{0.6}Sr_{0.2}Mn_{1.2-x}Cr_xO₃ perovskites with $x > 0$ become more complicated and are asymmetrically shifted to lower frequency. An analysis has shown that its wide line can be expanded into four lines centered around 319, 342, 373 and 404 MHz

(Fig. 3c). These components arise due to both different ionization states of the manganese ions and a non-equivalence of their crystallographic surrounding. The Cr^{3+} ions are most likely to substitute trivalent Mn ions in octahedral B positions. It is confirmed by a decrease of the NMR frequency of the Mn ions with increasing Cr content. In this case, the Cr ions partly suppresses an electron exchange between the Mn ions and the value T_C . As a result, the Mn ions with localized 3d-electrons are created. These are trivalent and tetravalent manganese ions with NMR lines centered at 319 and 404 MHz, respectively. The NMR line at 342 MHz should be related to manganese ions with intermediate valency.

4. CONCLUSIONS

1. We report a systematic study of FMR, SWR and NMR spectra in the La-deficient manganites with superfluous manganese content.
2. An anisotropy of FMR spectra determined from temperature and angular dependencies of both resonance field and linewidth is due to film-substrate strain effect. The large peak in the linewidth detected below the transition temperature is due to intrinsic phase separation when the film consists mainly of a FM matrix and embedded in the matrix AFM filamentary microdomains.
3. In epitaxial $\text{La}_{0.7}\text{Mn}_{1.3}\text{O}_3$ film the spin-wave resonance consisting of a seventeenth of standing spin-wave modes in the perpendicular magnetic field geometry has been observed. Two of them are the surface modes, while the others are the bulk spin-wave modes. The mode separation with angle observed in this study suggests that the boundary conditions are angular dependent. An unusual transformation of the spin-wave spectrum, namely, the disappearance of highest resonance modes with decreasing temperature have been found. Based on the temperature and angular dependencies data of SWR spectra, the spin-wave stiffness, exchange constant, g-factor value and saturation magnetization were estimated.
4. Numerical analysis of a wide asymmetrical line of the ^{55}Mn NMR spectrum in the $\text{La}_{0.6}\text{Sr}_{0.2}\text{MnCr}_{0.2}\text{O}_3$ compound enables its unique decomposition into four components with different resonance frequencies. These lines are due to both different valence states of the manganese ions and non-equivalence of their crystallographic surrounding in real structure. The NMR studies have shown that the Cr doping leads to a decrease of double exchange between manganese ions of different valencies.

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