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Electron spin resonance study of the magnetic states in the $Pr_{0.2}Sr_{0.8}Mn_{1-x}Ru_xO_3$ ($x = 0, 0.1$)

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Abstract

The effect of the substitution of ruthenium for manganese in a series of $Pr_{0.2}Sr_{0.8}MnO_3$ has been studied by electron spin resonance (ESR) for temperature ranging from 130 to 300 K. The ESR spectra display a single line in the whole temperature range. The temperature dependence of the line width and the effective g factor (g_{eff}) show the presence of the C-type antiferromagnetic to paramagnetic (AFM-PM) transition at about 275 K for both doped and undoped samples. The larger increase of g_{eff} for the composition $Pr_{0.2}Sr_{0.8}Mn_{0.9}Ru_{0.1}O_3$ was attributed to the presence of ferromagnetic (FM) interactions in the AFM state. Such a presence was confirmed by an increase of the magnetization values to $0.17\ \mu_B$ at 5 K.

Keywords: Perovskites; Electron spin resonance; Magnetic properties

Perovskite manganites with mixed manganese valence, $Ln_{1-x}AE_xMnO_3$ (Ln is a trivalent lanthanide, AE is a divalent alkaline-earth), demonstrate a rich variety of physical phenomena such as colossal magnetoresistance, charge and orbital ordering and phase separation. The electrical and magnetic properties can be modified by the substitution ions with different sizes and valence states at (Ln, AE) and Mn sites.[1–2] The electron spin resonance (ESR) was shown to be very sensitive to these magnetic properties and short-range interactions.[3] Occurrence of ferromagnetism and metallicity (FMM) responsible of the CMR properties in the compounds $Ln_{1-x}AE_xMnO_3$ are explained by the double exchange (DE) mechanisms between Mn^{3+} and Mn^{4+} species.[4] Recently, it was observed that the CMR effect was considerably modified when the FMM and antiferromagnetic insulator (AFMI) ground states compete to give a magnetic phase separation state at low temperature.[5] For Mn^{3+}-rich compounds, the substitution at the Mn site by a magnetic cation with a formal charge higher than 4+ showed the possibility to create FM in an AFM matrix, because not only it changes the carrier density but also introduces a change of interactions between Mn ions and the substituted cations.[6] Ru is a potential candidate to induce metallicity and ferromagnetism in these manganites due to its ability to adopt two valences Ru^{4+} and Ru^{5+}, which can both participate to strong super-exchange FM interactions with Mn^{3+}.[6–8] In this paper, we focus on the substitution of Ru for Mn in the $Pr_{0.2}Sr_{0.8}MnO_3$ manganites studied by electron spin resonance. [3,10]

Polycrystalline samples ($Pr_{0.2}Sr_{0.8}MnO_3$ and $Pr_{0.2}Sr_{0.8}Mn_{0.9}Ru_{0.1}O_3$) were prepared by an organic gel-assisted citrate process, followed by a thermal treatment under argon flow at 1250 °C for 12 h and an annealing under O_2 at 800 °C for 8 h. The powder X-ray diffraction patterns were recorded at room temperature by using a D8 diffractometer (θ–2θ) with a Cu Kα radiation. Crystallographic parameters were derived by the Rietveld method. X-band ($\nu \approx 9.5$ Ghz) ESR spectra, namely antiferromagnetic resonance at $T < T_N$ (Neel temperature) and paramagnetic resonance at $T > T_N$, were measured in a temperature range $130\ \mathrm{K} \leq T \leq 310\ \mathrm{K}$ with a Bruker ER 200 ESR spectrometer. Magnetization measurements were carried out using a Superconducting Quantum Interference

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Device (SQUID) in the temperature range 5–400 K during warming after a magnetic field of 1.45 T was applied at low temperature (zero field cooling process).

The undoped compound exhibits a weak tetragonal lattice distortion with the I4/mcm space group. The cell parameters and the volume refined with Fullprof program [11] are close to $a = 5.3992(2)$ Å, $c = 7.6434(5)$ Å and $V = 222.82(2)$ Å^3. The increase of both cell parameters and volume induced by Ru substitution corresponds to an increase of the tetragonal distortion with Ru content, without change of the space group.

Figs. 1 and 2 exhibit the temperature dependence of a few typical ESR signals for the $Pr_{0.2}Sr_{0.8}MnO_3$ and $Pr_{0.2}Sr_{0.8}Mn_{0.9}Ru_{0.1}O_3$ compounds. The evolution of the absorption signal curves is very similar for the both compounds. As the temperature decreases, the signal amplitude increases and reaches a maximum at 275 K and then decreases. This temperature corresponds to the transition temperature from paramagnetic state to antiferromagnetic state (PM-AFM), i.e. the Neel temperature. g_{eff} was calculated via $g_{\mathrm{eff}} = h\upsilon/\mu_B H_{\mathrm{res}}$, the linewidth ($\Delta H_{\mathrm{pp}}$) was deduced from the peak-to-peak distance between the maximum and the minimum of the derivative of the ESR absorption. They are shown, respectively, in Fig. 3a and b for $Pr_{0.2}Sr_{0.8}MnO_3$ and Fig. 4a and b for $Pr_{0.2}Sr_{0.8}Mn_{0.9}Ru_{0.1}O_3$. In the paramagnetic state, the central field at 300 K is equal to 3370 G corresponding to g_{eff} close to 2, which is a typical value of the free electron response for doped manganites in this magnetic domain. In this state, g_{eff} is independent of the temperature. The signals

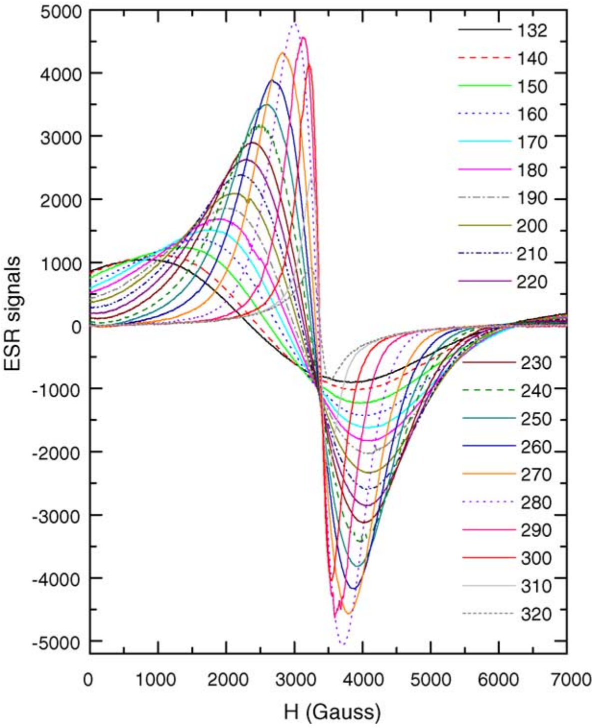

Fig. 1. ESR spectra of the $Pr_{0.2}Sr_{0.8}MnO_3$ sample measured from 130 to 320 K with a step of 10 K.

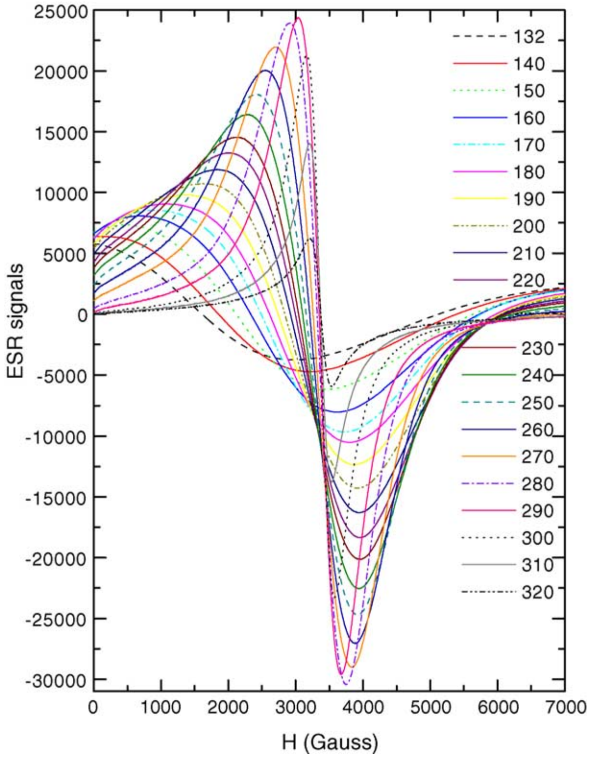

Fig. 2. ESR spectra of the $Pr_{0.2}Sr_{0.8}Mn_{0.9}Ru_{0.1}O_3$ compound measured from 130 to 320 K in a field from 0 to 7000 G.

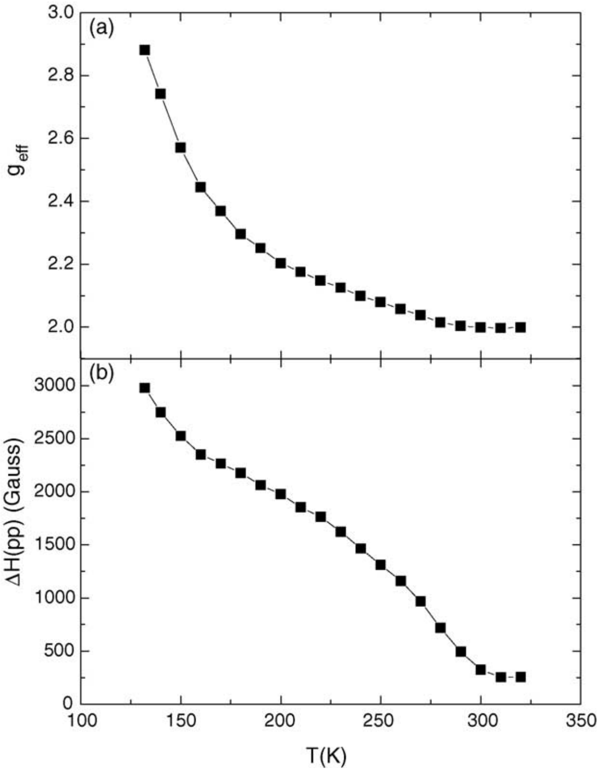

Fig. 3. Temperature variation line of the line shape parameters for $Pr_{0.2}Sr_{0.8}MnO_3$ compound, upper panel: g_{eff}-factor, lower panel: peak to peak linewidth ΔH_{pp}.

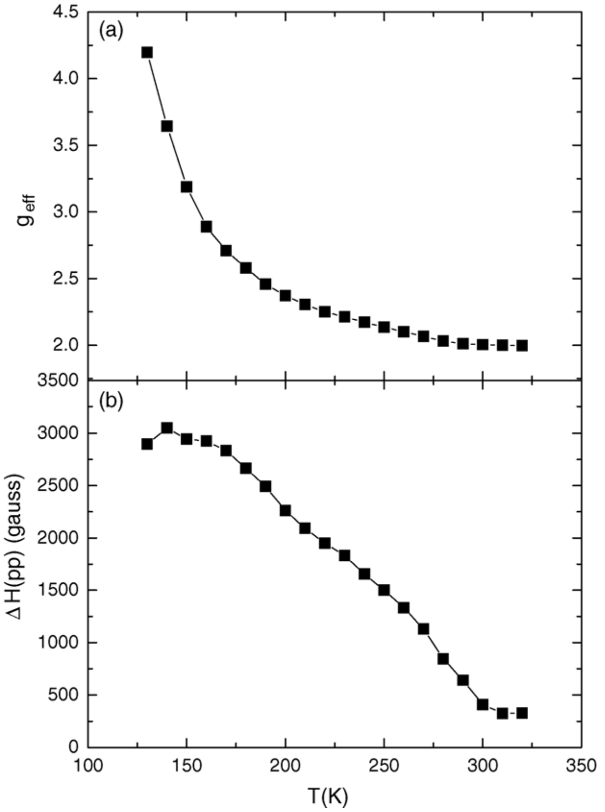

Fig. 4. Lineshape parameters for $Pr_{0.2}Sr_{0.8}Mn_{0.9}Ru_{0.1}O_3$: g_{eff}-factor (upper panel), linewidth (lower panel).

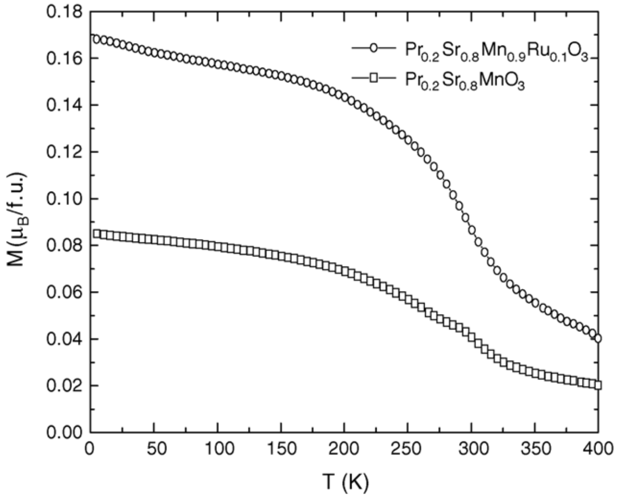

Fig. 5. T dependence of the magnetization (M) for $Pr_{0.2}Sr_{0.8}MnO_3$ and $Pr_{0.2}Sr_{0.8}Mn_{0.9}Ru_{0.1}O_3$ upon warming in a 1.45 T after a zero-field cooling down to 4 K.

show a relatively narrow ($\Delta H_{pp} \approx 250$ G) Lorentzian type line, which exhibits weak temperature dependence.

Below T_N, the spectra are characteristic of the antiferromagnetic resonance of the AFM ordered Mn moments.[3] The linewidth (ΔH_{pp}) increases gradually over the temperature range from 275 to 130 K due to the strong spin correlation (Figs. 3b and 4b). It can be noted that below T_N, the absorption line shifts from the centre field position and is asymmetric (Figs. 3a and 4a). g_{eff} increases from a value close to 2 up to reach 2.9 at $T = 130$ K for the undoped compound. But, the shift of the resonance line is weak, and contrary to what is observed in FM phases, the signal remains a single line. Indeed, if long-range FM domains existed in this material then the peak develops into two or three peaks at low and high field. The doped compound exhibits too a single line with a g_{eff} value which enhances up to a value close to 4.25 at 130 K, significant of the appearance of FM interactions in the compound.

This fact is in agreement with the magnetization measurements recorded at 1.45 T in a temperature range from 5 to 400 K (Fig. 5). The $M(T)$ curve of the $Pr_{0.2}Sr_{0.8}MnO_3$ compound shows that the magnetization at 4 K reaches a value close to 0.085 μ_B/f.u., confirming an AFM ordering of the Mn^{3+} and Mn^{4+} charges. However, a bump can be observed at 275 K and below this temperature the curve increases slightly, indicating the existence of a weak canting for the undoped compound. This bump was already observed in the literature and was explained as a signature of a charge carrier segregation phase.[12] This fact confirms the shift of the resonance field on the ESR curves (Fig. 1). The introduction of 10% Ru on Mn site leads to a slight increase of the magnetization at low temperature, up to a value close to 0.17 μ_B/f.u. (Fig. 3), that shows that FM interactions are induced by the substitution within the AFM matrix. But the FM interactions remain weak in these doped manganites, indicating that the Ru do not generate a long-range FM order in the matrix.

The ferromagnetism can be explained by the Ru for Mn substitution, which induces Mn^{3+} species in the $Pr_{0.2}{}^{3+}Sr_{0.8}{}^{2+}Mn_{0.2}{}^{3+}Mn_{0.8}{}^{4+}O_3$ compound and thus allows Mn^{3+}–O–Mn^{4+} DE interactions to develop in the AFM matrix. For that, the Ru must adopt an oxidation state superior than (IV) to create some Mn^{3+} species.[13] But, the Ru effect is weak compared with compounds containing the same ratio Mn^{3+}/Mn^{4+} and Ru for example $Sm_{0.2}Ca_{0.8}Mn_{0.9}Ru_{0.1}O_3$.[9] In comparing the Ru effect in $Sm_{0.2}Ca_{0.8}Mn_{0.9}Ru_{0.1}O_3$ and $Pr_{0.2}Sr_{0.8}Mn_{0.9}Ru_{0.1}O_3$, the moment value reaches 1.7 μ_B/f.u. and 0.17 μ_B/f.u. at 4 K, respectively. Both samples display the same magnetic structure (C-type) at low temperature, but $Sm_{0.2}Ca_{0.8}MnO_3$ is near a cluster glass transition, which makes the appearance of FM by Ru doping easier.

The ESR data evidences that Ru-doping modifies the magnetic ordered states and creates a phase separation magnetic state in $Pr_{0.2}Sr_{0.8}Mn_{0.9}Ru_{0.1}O_3$. Further investigations on other compositions and other substitutions are in area to support these results.

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