

## Peculiar features of electron spin resonance spectra in (Ca,Na)-doped lanthanum manganites

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The analysis of the ESR spectra for the powdered samples of (Ca,Na)-doped manganites have been performed in the temperature range 220–320 K. It is shown that the samples under investigation are characterized by a broadened para- to ferromagnetic transition and complicated spectra within the transitional region. The conclusion is made that the satisfactory interpretation of the resonance data is only possible if the interference of the coexisting phases is taken into account within the transitional region. Under these conditions, the resonance field for the paramagnetic phase is shown to increase with the temperature lowering, while that for the ferromagnetic phase first decreases and then approaches a value characteristic of the uniformly magnetized ferromagnetic sample. It is noted that the results obtained are in compliance with those predicted theoretically for the spherical particles containing a mixture of the paramagnetic and ferromagnetic phases.

PACS: **76.50.+g** Ferromagnetic, antiferromagnetic, and ferrimagnetic resonances; spin-wave resonance;  
75.30.Kz Magnetic phase boundaries (including magnetic transitions, metamagnetism, etc.);  
75.47.Gk Colossal magnetoresistance.

Keywords: electron spin resonance, magnetic phase coexistence, doped lanthanum manganites.

Electrically conducting ferromagnetic materials where the conduction electrons have a high mobility and are fully spin-polarized are desirable for realizing thin-film spin electronic devices [1,2]. The doped manganite systems  $\text{La}_{1-x}\text{M}_x\text{MnO}_3$  ( $\text{M}$  = alkaline or alkaline earth element), due to their half-metallic ferromagnetic nature and the concomitant complete spin polarization, have been considered as very promising materials for the creation of spin emitters and filters in magnetic nanostructures.

Recent theoretical and experimental studies have shown that the essential physics of doped manganites stems from a strongly pronounced tendency towards magnetic phase separation, which often makes an inhomogeneous state more preferable than a homogeneous one [3–5]. Electron spin resonance (ESR) is an advantageous tool to probe the manganite behavior within the regions of phase coexistence but the interpretation of the results is far from being unambiguous [6–8]. It is the mutual influence of coexisting phases that may strongly change the resonance conditions for each of the coexisting phases [6,9,10].

The analysis of the behavior of the system in which paramagnetic (PM) and ferromagnetic (FM) phases coex-

ist over a wide temperature range was carried out in Refs. 6 and 10. Drastic transformations of the resonance spectra are predicted for the region of the phase coexistence. The fact that the FM phase doesn't occupy the whole volume of a particle changes the resonance conditions for the FM phase, as they in the first place are governed by the shape of FM regions [11]. On the other hand, the magnetic fields created by the FM regions strongly transform the resonance conditions for the PM phase [6,10].

To date, there have been only few works with the reasonable interpretation of experimental data within the temperature range where the FM and PM phases coexist [6,9,12,13]. To clarify the picture, one should carry out a comprehensive analysis of the ESR spectra on the carefully characterized samples with a broadened magnetic transition. As follows from the studies of magnetic properties, the most suitable samples for this aim are Ca- and Na(K)-doped lanthanum manganites, the peculiar feature of which is a wide temperature range of the PM and FM phases coexistence [14–17]. Here, we present the results of the ESR measurements in (Ca,Na)-doped lanthanum manganites, which clearly show that coexisting phases

cannot be considered as independent and their mutual influence should be taken into account.

To extend the width of the magnetic transition, we synthesized the samples with the excessive amount of structural vacancies in a lanthanum sublattice. To do this, the bulk polycrystalline samples with the nominal chemical formula  $\text{La}_{0.7+x}\text{Ca}_{0.3-2x}\text{Na}_x\text{MnO}_3$  were prepared, where the substitution was made according to the scheme  $2\text{Ca} \rightarrow \text{La} + \text{Na}$ . The reason for the vacancy formation was enhanced sodium volatility at high temperatures [15]. The details of the samples' preparation and characterization are described in Refs. 15, 16, 18. The ESR investigations were performed on the powdered samples with  $x = 0.04$  and 0.08. The powder consisted of micrometer-sized particles whose shape was close to the spherical one. The measurements were carried out with the use of X-band EPR spectrometer Radiopan SE/X-2544 (operating frequency  $\nu \approx 9.2$  GHz) in the temperature range 220–320 K.

Figures 1 and 2 show the features of the temperature evolution of the ESR spectra for the sample with  $x = 0.04$ . In a high-temperature region ( $T > 304$  K), the spectrum consists of a single symmetric line L1 which keeps discernible down to 280 K. At  $T = 320$  K, the integrated curve is well fitted by a Lorentzian with the parameters

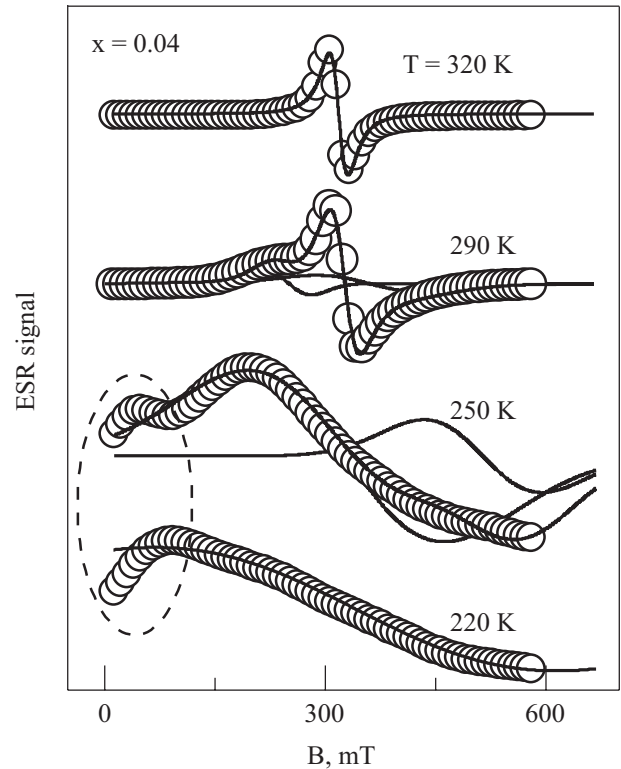


Fig. 2. Experimental (open circles) and fitted (solid lines) resonance curves for the sample with  $x = 0.04$ .

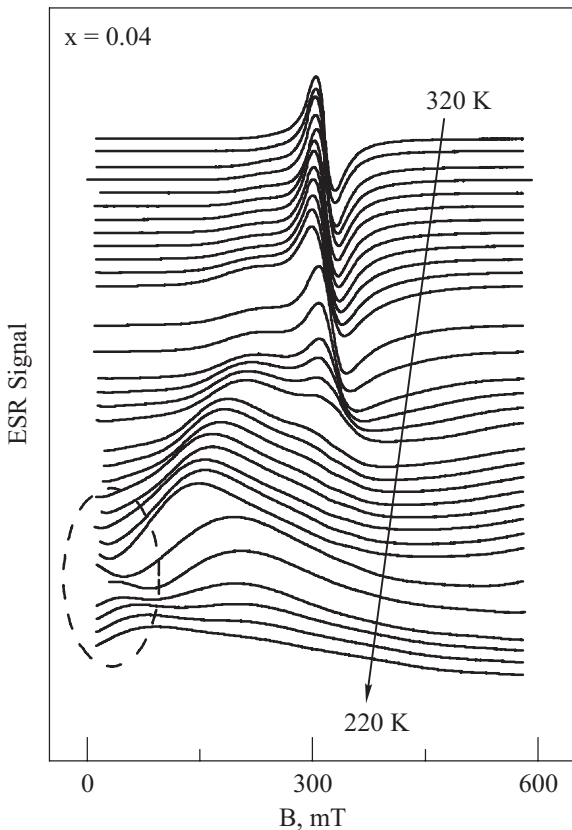


Fig. 1. Temperature evolution of the ESR spectra for  $\text{La}_{0.7+x}\text{Ca}_{0.3-2x}\text{Na}_x\text{MnO}_3$  with  $x = 0.04$ . A dashed ellipse marks the low-field line which is not subjected to the analysis in this work.

which correspond to the paramagnetic state of manganites (resonance field  $B_0^{L1} \approx 318$  mT, linewidth  $w^{L1} \approx 44$  mT) [9,10,12]. With the temperature lowering, the resonance field of this line remains almost constant, but the linewidth gradually increases. As  $T$  crosses 304 K, the integrated curve deviates from the Lorentzian. The analysis shows that the experimental curve cannot be decomposed into two lines any longer: a satisfactory description can only be achieved when one involve three lines — L1 and two additional ones (see Fig. 2). These additional lines have the shape of Gaussians with the resonance fields higher (L2) and lower (L3) than  $B_0^{L1}$ . With the further decrease in temperature, the intensity of L1 diminishes and the spectra can be satisfactory described as consisting of the lines L2 and L3 ( $240 \text{ K} \leq T < 280 \text{ K}$ ) or L3 only ( $T < 240 \text{ K}$ ). At  $T < 274 \text{ K}$  another, low-field line appears (marked by dashed ellipses in Figs. 1 and 2), the nature of which was discussed in Refs.19–21. The analysis of its behavior is beyond the frames of this work.

It should be noted that the spectra consisting of two Gaussians, one being centered at  $B > B_0^{L1}$  and another at  $B < B_0^{L1}$ , were predicted in Ref. 10 for a spherical particle containing a mixture of the PM and FM phases. In our case, the coexistence of these lines with L1 may imply that although the FM phase is nucleated in some of the powder particles, the rest of them still remains purely paramagnetic within a certain temperature range.

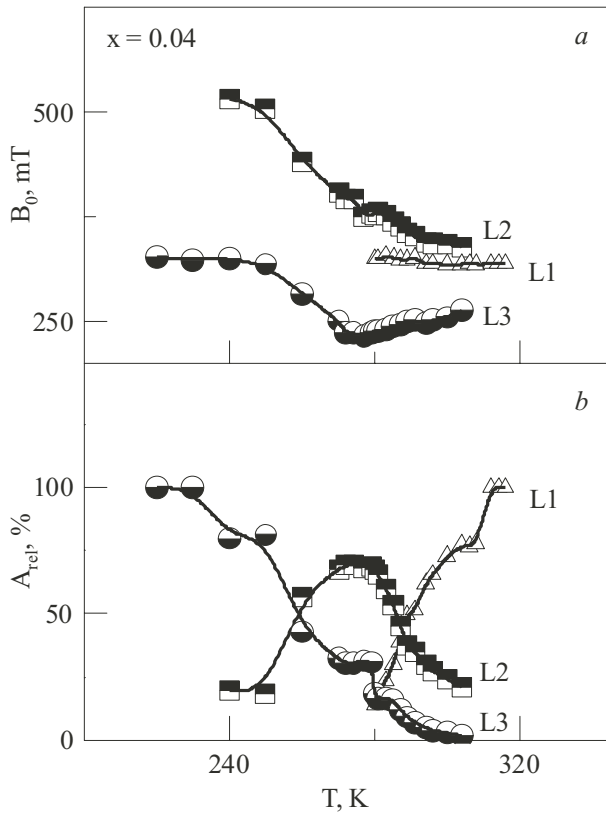


Fig. 3. Resonance fields (a) and relative intensities (b) of the lines L1–L3 for  $\text{La}_{0.7+x}\text{Ca}_{0.3-2x}\text{Na}_x\text{MnO}_3$  with  $x = 0.04$ .

Analyze the behavior of the ESR spectra in more details. Figure 3,a shows the temperature dependences of the resonance fields for the lines L1–L3. As was noted above,  $B_0^{L1}$  remains almost constant and doesn't exhibit noticeable changes with temperature. On the contrary, the resonance fields for the other two lines undergo drastic changes. With the temperature lowering,  $B_0^{L2}$  displays a monotonic increase, but  $B_0^{L3}$  first decreases, reaches a minimum, then grows and eventually keeps almost constant after reaching the value which is close to  $B_0^{L1}$ . It is noteworthy that a similar picture was also reported in Ref. 12 for the powdered bulk samples of  $(\text{La,Pr,Pb})\text{Mn}_{1-x}\text{Cu}_x\text{O}_3$ .

After the integrated spectrum was decomposed into  $N$  lines and the area  $A^{Li}$  under  $i$ th line was found, the relative intensity of each of the lines was calculated according to the formula:  $A_{rel}^{Li} = A^{Li} / \sum_{i=1}^N A^{Li}$ . Figure 3,b shows the

values of  $A_{rel}^{Li}$  as functions of temperature. It is seen that for the temperatures beyond the transitional region (240–304 K), the ESR spectrum consists of a single line, namely, L1 at high temperatures or L3 at low temperatures. This allows us to associate the line L1 with the PM phase and L3 with the FM one. Within the transitional region, the temperature dependences of the relative intensity of these lines display the monotonic and opposite

trends, as is expected for the case of a broadened PM to FM transition. The behavior of the line L2 which exists only within the transitional region is somewhat unusual and its nature needs to be discussed further.

The analysis of the ESR spectra for a spherical particle in which the PM and FM phases coexist over a wide temperature range was carried out in Ref. 10. It was shown that the mutual influence of the coexisting phases results in the following effects: the resonance field for the PM phase increases with the temperature lowering, while that for the FM phase first decreases and then approaches a value characteristic of the uniformly magnetized ferromagnetic sample. Applying this scenario to our case, we should expect that, since the shape of the particles is close to the sphere, the resonance field for the line L3 should approach  $B_0^{L1}$  at low temperatures [11], and this is actually observed in experiment (see Fig. 3,a). As is also seen from Fig. 3, the behavior of L2 well agrees with what is predicted for the paramagnetic resonance signal for the case where the PM phase coexists with the FM one and senses the action of its effective field [10]. The line L1, as was noted above, originates from the particles which are purely paramagnetic.

When the transition is extremely broadened, the lines L2 and L3 can coexist down to the lowest temperatures. It seems that Fig. 4 reflects just this case. For the sample  $\text{La}_{0.7+x}\text{Ca}_{0.3-2x}\text{Na}_x\text{MnO}_3$  with  $x = 0.08$ , the intensities of the lines L2 and L3 are comparable at the lowest tempera-

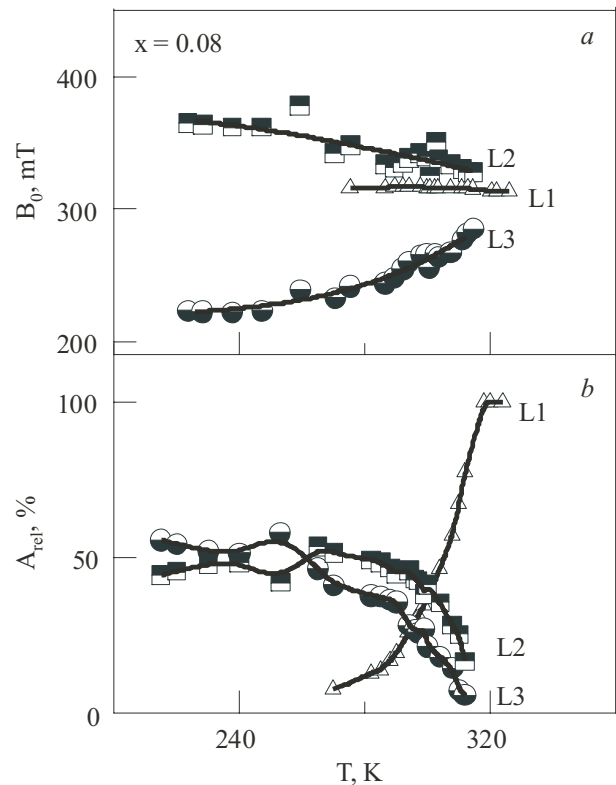


Fig. 4. Resonance fields (a) and relative intensities (b) of the lines L1–L3 for  $\text{La}_{0.7+x}\text{Ca}_{0.3-2x}\text{Na}_x\text{MnO}_3$  with  $x = 0.08$ .

tures achievable in our measurement setup (220 K) and, thus, we were unable to observe the situation where L3 becomes dominant. It is noteworthy that similar results were reported by other research groups on a number of the doped manganite compounds [6,9,12,13,19].

In summary, the analysis of the ESR spectra for the powdered samples of  $\text{La}_{0.7+x}\text{Ca}_{0.3-2x}\text{Na}_x\text{MnO}_3$  with  $x = 0.04$  and  $0.08$  have been performed over a wide temperature range. It is shown that for the temperatures beyond the transitional region, the integrated curve is well described by a single line, namely, by the Lorentzian in the purely PM state and the Gaussian in the purely FM state. Within the transitional region, the resonance spectra become more complicated and this especially concerns the particles, in which the PM and FM phases coexist. In the latter case, the reasonable interpretation of the observed spectra is only possible when the interference of the coexisting phases is taken into account. Under these conditions, the resonance field for the PM phase increases with the temperature lowering, while that for the FM phase first decreases and then approaches a value characteristic of the uniformly magnetized ferromagnetic sample, which is in compliance with the results predicted in Ref. 10 for the spherical particles containing a mixture of the PM and FM phases.

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