Interference of coexisting para- and ferromagnetic phases in partially crystallized films of doped manganites

Interference of coexisting para- and ferromagnetic phases in partially crystallized films of doped manganites

A I Tovstolytkin[1,3]**, A M Pogorily**[1]**, Yu I Dzhezherya**[1]**, V V Dzyublyuk**[1] **and D J Mapps**[2]

[1] Institute of Magnetism, 36-b Vernadsky Boulevard, Kyiv 03142, Ukraine
[2] Centre for Research in Information Storage Technology, University of Plymouth, Plymouth PL4 8AA, UK

E-mail: atov@imag.kiev.ua

Abstract
Electron spin resonance spectra have been studied in partially crystallized films of
$La_{1-x}Na_xMnO_3$ ($x = 0.16$) in the vicinity of the para- to ferromagnetic transition. The objects
of investigation were obtained by magnetron sputtering on polycrystalline Al_2O_3 substrates held
at different temperatures. It is shown that, in a regime where the paramagnetic and
ferromagnetic phases coexist, the resonance conditions for one phase strongly depend on the
parameters of the other phase. As a result, the resonance field of the paramagnetic phase
becomes dependent on the shape of the sample, the saturation magnetization and the fraction of
the ferromagnetic phase. A simple model is developed to predict the character of the changes in
the resonance field of the paramagnetic phase upon the nucleation of the ferromagnetic phase.

1. Introduction

The materials, in which magnetically ordered and disordered components coexist, have drawn more and more attention in recent years [1–3]. The coexistence of such types may be created artificially or it may reflect the intrinsic tendency towards magnetic phase separation [4–6]. The research effort is primarily directed towards the investigation of the behaviour of the magnetically ordered component; its action on the magnetically disordered one is usually neglected. This, however, is inadmissible for the case where magnetic resonance is studied in the system, since the fields induced by the former can strongly modify the resonance conditions for the latter [7, 8].

The analysis of the behaviour of the system in which paramagnetic (PM) and ferromagnetic (FM) phases coexist over a wide temperature range was carried out in [9]. Drastic transformations of the resonance spectra were predicted for the region of phase coexistence. The fact that the FM phase does not occupy the whole volume of a sample changes the resonance conditions for the FM phase, as, in the first place,

they are governed by the shape of the FM regions. On the other hand, the magnetic fields created by the FM regions strongly transform the resonance conditions for the PM phase [7–9].

To date, there have been only a few works with a reasonable interpretation of experimental data within the temperature range where the FM and PM phases coexist [7, 10–12]. To clarify the picture, one should carry out a comprehensive analysis of the electron spin resonance (ESR) spectra in 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 [13–17]. The other advantage of such films is that their properties can be widely varied by means of the variation of their fabrication conditions [18].

It was shown in [9] that the features of the phase interference strongly depend on a sample shape. The case of a spherical sample was analysed in detail but for slabs or thin films this effect was studied neither theoretically nor experimentally. Here, we present the results of the ESR measurements on two partially crystallized films of sodium-doped manganites, which clearly show that the coexisting

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[3] Author to whom any correspondence should be addressed.

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

2. Experimental details

Thin films of $La_{1-x}Na_xMnO_3$ (x = 0.16) with a thickness d = 250 nm and dimensions 3 mm × 12 mm were prepared on polycrystalline Al_2O_3 substrates by DC magnetron sputtering [18]. A ceramic target for thin film preparation was fabricated by a conventional solid-state reaction method [14, 19]. The studies were carried out on films obtained at two different substrate temperatures, 300 °C and 500 °C (films 1 and 2, respectively). Both films were prepared in a mixture of argon (30%) and oxygen (70%). The gas pressure during the deposition was 2×10^{-2} Torr. After the deposition, the films were subjected to a heat treatment at 600 °C in an ambient atmosphere. The duration of the heat treatment was 4 h. It was concluded earlier that manganite films subjected to such a kind of heat treatment are partially crystallized, with the relative amount of amorphous/crystalline phase being dependent on the conditions of the heat treatment [18, 20].

The magnetic resonance studies were carried out in the temperature range 220–290 K with the use of an X-band EPR spectrometer Radiopan SE/X-2544 (operating frequency $\nu \cong$ 9.2 GHz). The measurements were performed for the cases where the magnetic field was parallel and perpendicular to a film plane.

3. Results and discussion

Temperature evolution of the differential absorption curves, dI/dH, for films 1 and 2 is shown in figures 1 and 2, respectively. In both cases, a spectrum at 290 K consists of a wide line located near 3115 Oe and a narrow one near 1240 Oe. The latter line, along with a few smaller lines in its vicinity, originates from an Al_2O_3 substrate. The position of these lines is almost independent of temperature. The former line (line 1) belongs to the manganite film and it undergoes strong modifications upon temperature change. As temperature is lowered, this line becomes more intense with respect to the lines from the substrate and eventually the peaks from the substrate are almost indiscernible.

For both films, the resonance fields of line 1, H_{r1}, are identical and the position of the line does not depend on the orientation of the external magnetic field H with respect to the film plane. The value of the resonance field corresponds to $g_{eff} \approx 2$, which is a typical value of the free-electron response for doped manganites [10, 11]. g_{eff} was calculated via $g_{eff} = h\nu/(\mu_B H_{r1})$, where ν is the frequency of the electromagnetic wave, h is Planck's constant and μ_B is the Bohr magneton. The linewidths, deduced from the peak-to-peak distances between the maximum and minimum on the dI/dH curves, are 457 and 462 Oe for films 1 and 2, respectively.

With the decrease in temperature, the position of line 1 remains independent of both temperature and field orientation until a certain temperature T_{c1} is crossed (T_{c1} = 270 K and 250 K for films 1 and 2, respectively). At $T \leqslant T_{c1}$, a second
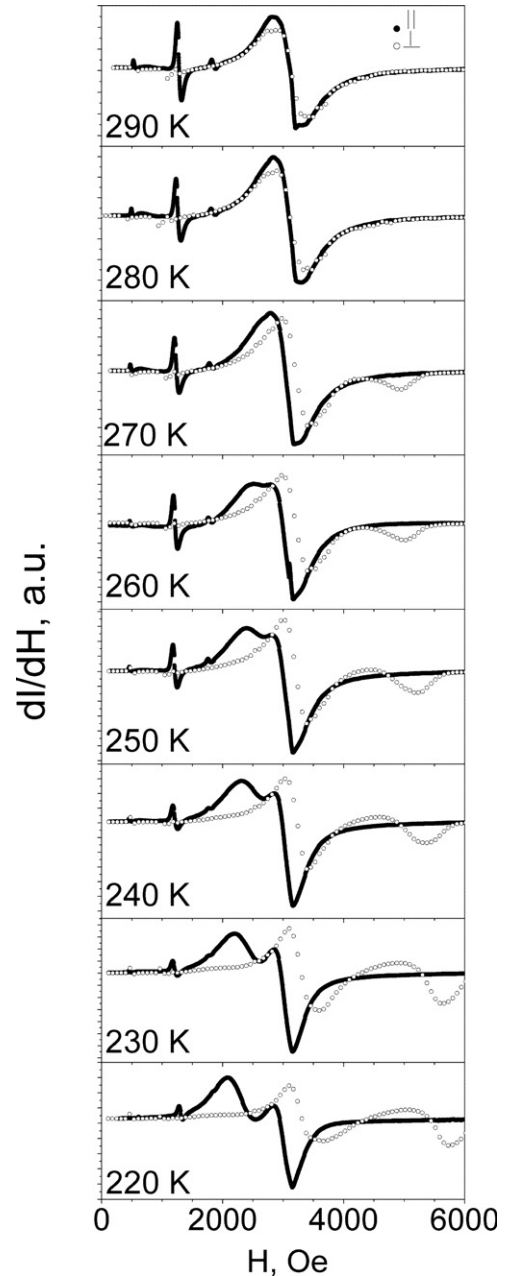

Figure 1. Differential absorption curves dI/dH versus H for the $La_{1-x}Na_xMnO_3$ ($x = 0.16$) film fabricated at $T_s = 300$ °C.

line appears and the spectra undergo drastic transformations. The resonance field of line 2, H_{r2}, is dependent on the orientation of H. In particular, H_{r2} is greater than H_{r1} if H is perpendicular to a film plane (perpendicular case) and, vice versa, it is less than H_{r1} if H is parallel to the film plane (parallel case). As the temperature is lowered, the intensity of this line grows and it moves away from line 1.

Before turning to a detailed analysis of the transformation of the resonance spectra with temperature, let us make the following remarks. It is known that the resonance spectrum of an FM sample is strongly dependent on the orientation of the external magnetic field, contrary to the case of a PM one. The reason for this is a strong shape anisotropy characteristic of a finite FM sample. The resonance fields for a thin FM film can
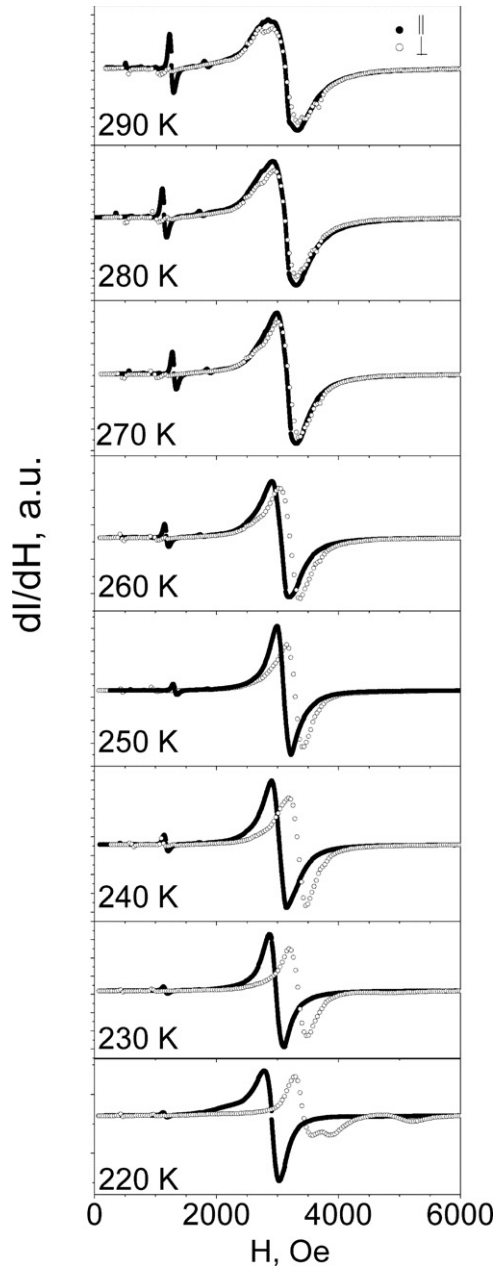
Figure 2. Differential absorption curves $\mathrm{d}I/\mathrm{d}H$ versus H for the $La_{1-x}Na_xMnO_3$ ($x = 0.16$) film fabricated at $T_s = 500\,^\circ C$.

be estimated from the Kittel formulae (see, for example, [21]). It follows from these formulae that the position of the FM resonance line is dependent on the orientation of H, namely the line is located at a higher (perpendicular case) or lower (parallel case) magnetic field with respect to the position of the PM resonance line with $g_{eff} \approx 2$.

Thus, in our case, lines 1 and 2 can be identified as the lines originating from the PM and FM phases, respectively. With the decrease in temperature, the position of line 2 is changed, which reflects the increase in the sample magnetization, as is usually observed in FM samples [11, 17, 21]. A striking feature, however, is that, at $T \leqslant T_{c1}$, the position of line 1 is also dependent on the external field orientation, and this dependence becomes more pronounced as temperature is lowered.

To analyse the evolution of the spectra in more detail, we plotted the integrated absorption spectra $I(H)$ (figures 3 and 4 for films 1 and 2, respectively). At $T > T_{c1}$, each integrated curve is described with good accuracy by a Lorentzian centred at H_{r1}. The value of H_{r1} is temperature-independent. Each curve at $T \leqslant T_{c1}$ is well described as a superposition of a Lorentzian and Gaussian centred at H_{r1} and H_{r2}, respectively. In the range of the PM and FM phase coexistence, the resonance fields for both phases are dependent on temperature and field orientation. It is noteworthy that a shift of the PM resonance field in the presence of the FM phase was also observed in $La_{1-x}Ca_xMnO_3$ ($x = 0.3$ and 0.5) single-crystalline samples [7, 22] and $La_{0.73}Ca_{0.27}MnO_3$ epitaxial films [10]. However, the authors did not give an adequate explanation why the resonance conditions for the PM phase are changed in the presence of the FM phase.

Figures 5 and 6 show the dependences of the resonance fields H_{r1} and H_{r2} versus temperature for films 1 and 2, respectively. At sufficiently high temperatures ($T > T_{c1}$), the resonance field of the PM phase, H_{r1}, does not depend on temperature and magnetic field orientation. However, at temperatures lower than the temperature of the FM phase nucleation ($T < T_{c1}$), H_{r1} for the perpendicular case differs from that for the parallel case, and this difference is increased as temperature decreases.

Here, we should note that, although T_{c1} for film 2 is less than that for film 1, the intensity of the FM resonance line grows much more rapidly in the former film. The same tendency is also characteristic of the sensitivity of the resonance fields to the orientation of the external magnetic field. All these facts imply that, in film 1, the PM to FM transition is strongly broadened. In contrast, in film 2, the transitional range is much narrower. Such conclusions well agree with those obtained in work [18] which reported the effects of a substrate temperature and post-deposition heat treatment on the transport and magnetoresistance properties of $La_{1-x}Na_xMnO_3$ ($x = 0.16$) films. It was concluded in this work that, on the one hand, the enhanced heat treatment gave rise to a narrowing of the resistive/magnetic transitions, as a result of the improved crystallinity and structural homogeneity of the samples. On the other hand, it led to the decrease in the magnetic transition temperature, with the effect originating from a change in a sample stoichiometry caused by the high volatility of sodium.

Thus, to summarize the results of the experimental part, it is shown that, for the case where the PM and FM phases coexist, the presence of the latter influences the resonance conditions for the former. In what follows, we will try to describe the mechanism of such an influence, based on a simple model.

Consider a PM matrix which contains inclusions of an FM phase. The frequency of the PM resonance within a small chosen volume is determined as

$$w_{PMR} = \gamma\sqrt{(\mathbf{H} + \mathbf{h})^2}, \qquad (1)$$

where $\gamma = 2\mu_B/\hbar$, $\mathbf{H}$ is the external field and $\mathbf{h}$ is the field of dipole origin, induced by the clusters of the FM phase. Here, a dipole contribution from the PM matrix is neglected.
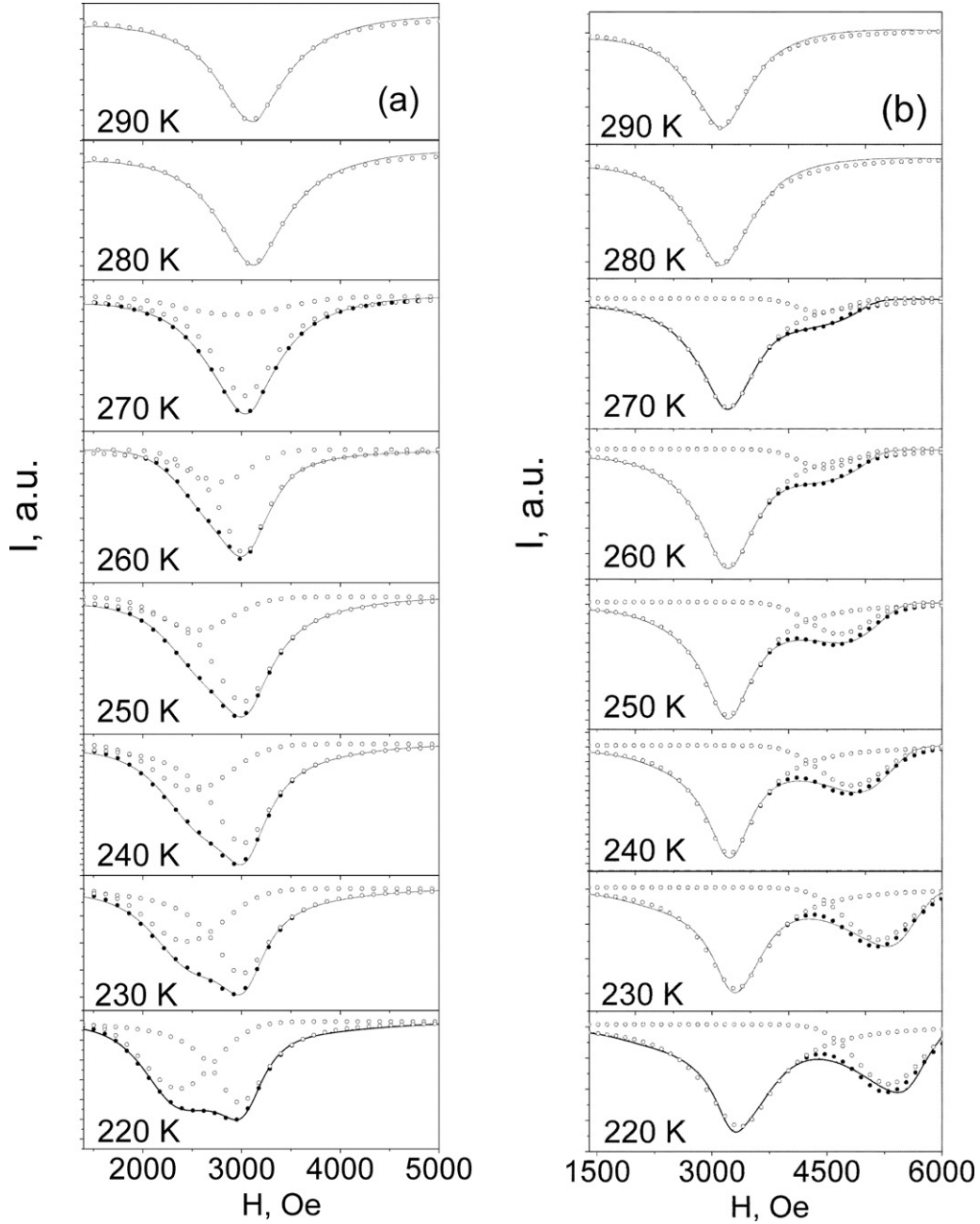
Figure 3. Integrated curves of magnetic resonance, $I(H)$, for the parallel (a) and perpendicular (b) orientation of the plane of film 1 with respect to the external magnetic field. Solid lines show experimental data, open circles the results of the decomposition into one ($T > 270$ K) or two ($T \leqslant 270$ K) absorption lines.

At the early stage of the FM phase nucleation, when the FM fraction is small, the magnetodipole contribution from the FM clusters is also small compared with the external field magnitude. Thus, the expression on the right-hand side of equation (1) can be developed in a series in **h** and the development can be restricted to a first-order term. As a result, the PM resonance frequency can be written in the form

$$w_{\text{PMR}} \approx \gamma H + \gamma (\mathbf{e} \cdot \mathbf{h}), \qquad (2)$$

where $H = |\mathbf{H}| = \text{const}$ and $\mathbf{e} = \mathbf{H}/H$ is the unit vector in the direction of the external magnetic field. After averaging over the volume of the PM phase, the above expression can be

written as

$$\langle w_{\text{PMR}} \rangle \approx \gamma H + \gamma (\mathbf{e} \cdot \langle \mathbf{h} \rangle_{\text{PM}})$$

$$\langle \mathbf{h} \rangle_{\text{PM}} = V_{\text{PM}}^{-1} \int_{V_{\text{PM}}} d\upsilon \, \mathbf{h} \qquad (3)$$

where $\langle \mathbf{h} \rangle_{\text{PM}}$ is the average magnetic field induced by the FM clusters in the PM matrix and V_{PM} is the volume of the PM phase. It is seen that a nonzero contribution occurs only from that component of **h** which is parallel to the external magnetic field.

To go further, let us consider a sample of an ellipsoidal shape. If the sample is magnetized along an ith axis of the
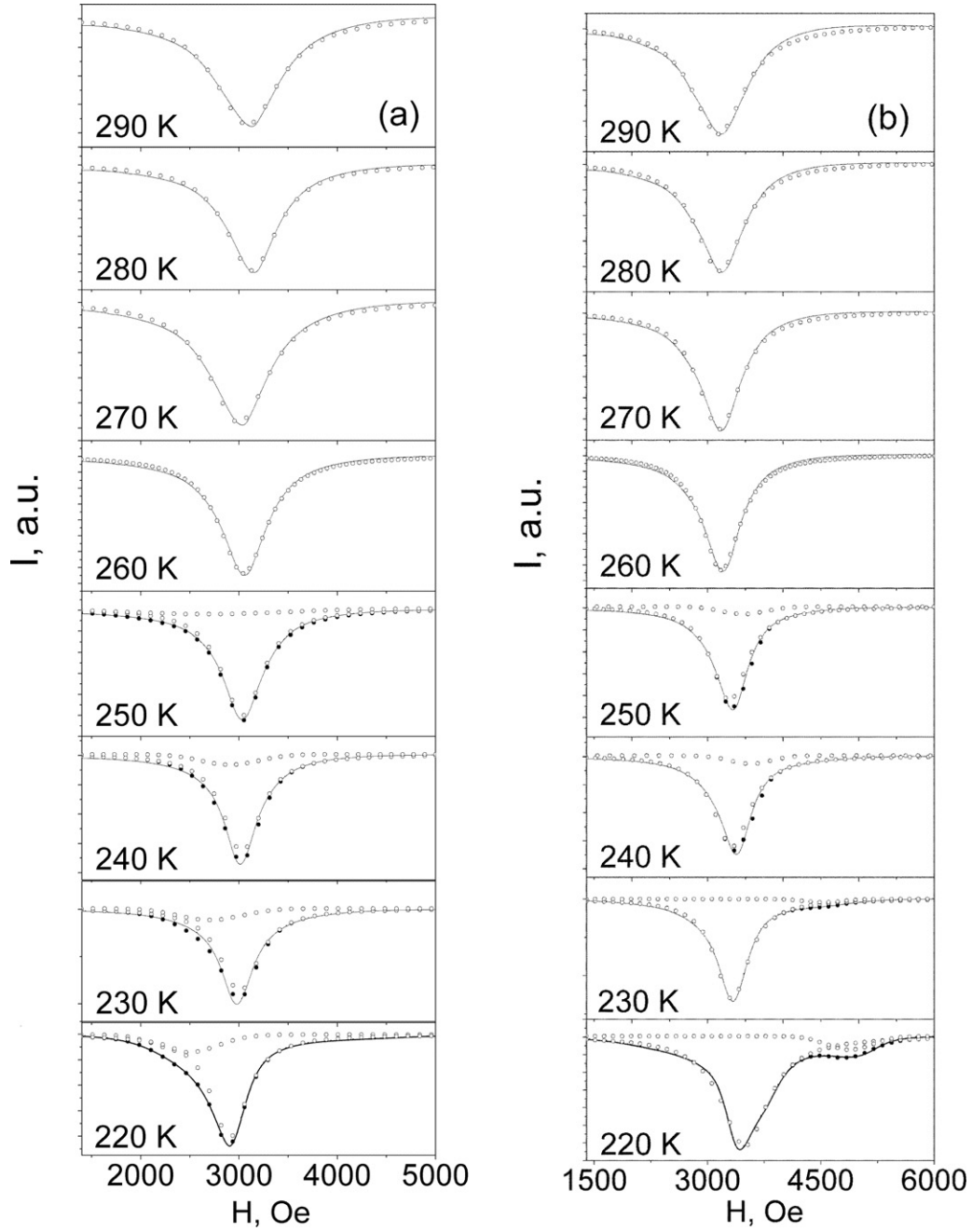
Figure 4. Integrated curves of magnetic resonance, $I(H)$, for the parallel (a) and perpendicular (b) orientation of the plane of film 2 with respect to the external magnetic field. Solid lines show experimental data, open circles the results of the decomposition into one ($T > 250$ K) or two ($T \leqslant 250$ K) absorption lines.

ellipsoid, the average magnetostatic field inside the sample is

$$\langle h_i \rangle = -4\pi N_i \langle M \rangle, \tag{4}$$

where N_i is the demagnetization coefficient along the ith axis and $\langle M \rangle$ is the average magnetization of the sample:

$$\langle M \rangle = \frac{V_{\mathrm{FM}}}{V_{\mathrm{FM}} + V_{\mathrm{PM}}} M_0. \tag{5}$$

Here, V_{FM} is the volume occupied by the FM phase and M_0 is its saturation magnetization.

On the other hand, the average magnetic field inside the sample can be calculated as

$$\langle h_i \rangle = \frac{1}{V} \int_V \mathrm{d}\upsilon\, h_i$$
$$= \frac{1}{V_{\mathrm{FM}} + V_{\mathrm{PM}}} \left(\int_{V_{\mathrm{PM}}} \mathrm{d}\upsilon\, h_i + \int_{V_{\mathrm{FM}}} \mathrm{d}\upsilon\, h_i \right). \tag{6}$$

It was shown in paper [9] that, in the case where the PM phase prevails, it is favourable for the FM clusters to take the shape which is close to the ellipsoid of rotation with a long axis parallel to the direction of the external magnetic field. In this
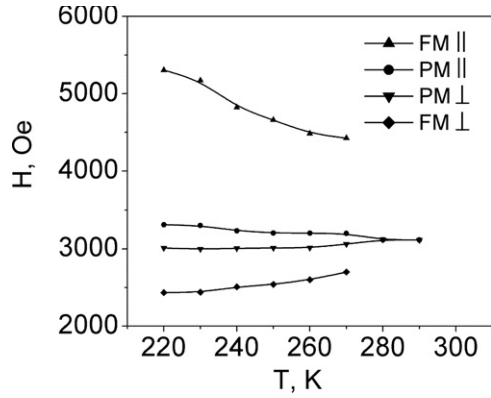
Figure 5. Temperature dependence of the resonance fields for two orientations of the plane of film 1 with respect to the external magnetic field.

Figure 6. Temperature dependence of the resonance fields for two orientations of the plane of film 2 with respect to the external magnetic field.

case, the second term in expression (6) can be easily calculated:

$$\frac{1}{V_{\mathrm{FM}} + V_{\mathrm{PM}}} \int_{V_{\mathrm{FM}}} \mathrm{d}\upsilon\, h_i = \langle h_i \rangle_{\mathrm{FM}}$$
$$= -4\pi M_0 \sum_a \frac{\upsilon_a n_a}{V_{\mathrm{FM}} + V_{\mathrm{PM}}}, \tag{7}$$

where υ_a and n_a are the volume and demagnetization coefficient, respectively, of a cluster number a. With regards to (4) and (7), expression (6) can be rewritten as

$$\langle h_i \rangle - \langle h_i \rangle_{\mathrm{FM}} \equiv \langle h_i \rangle_{\mathrm{PM}} = \langle h_i \rangle + 4\pi M_0 \sum_a \frac{\upsilon_a n_a}{V_{\mathrm{FM}} + V_{\mathrm{PM}}}. \tag{8}$$

Consider a case where n_a is the same for all the FM clusters. Then, $\sum_a \frac{\upsilon_a n_a}{V_{\mathrm{FM}} + V_{\mathrm{PM}}} = n_a \sum_a \frac{\upsilon_a}{V_{\mathrm{FM}} + V_{\mathrm{PM}}} = \frac{V_{\mathrm{FM}}}{V_{\mathrm{FM}} + V_{\mathrm{PM}}}$. With regard to expressions (4) and (5), $\langle h_i \rangle_{\mathrm{PM}}$ is

$$\langle h_i \rangle_{\mathrm{PM}} = -4\pi M_0 f (N_i - n_a), \tag{9}$$

where $f = V_{\mathrm{FM}}/(V_{\mathrm{FM}} + V_{\mathrm{FM}})$ is the volume fraction of the FM phase.

The results obtained can be used to determine the character of the changes in the PM resonance field upon the nucleation of the FM phase. The resonance field can be calculated from expressions (3) and (9):

$$H_{\mathrm{r1}} \approx H_w + 4\pi M_0 f (N_i - n_a), \tag{10}$$

where $H_w = \langle w_{\mathrm{PMR}} \rangle / \gamma$. Thus, the resonance field of the PM phase becomes dependent on the shape of the sample, the saturation magnetization and the fraction of the FM phase. It should be noted that this expression is more accurate than that obtained in paper [9], where the term containing n_a was taken into account only at the final stage of the magnetic transition but not at the initial one.

Let us consider a case where the sample is a thin film and the shape of the clusters is spherical ($n_a = 1/3$), which is often observed at the early stage of the FM phase nucleation [23]. Under these conditions, the expressions for the PM resonance
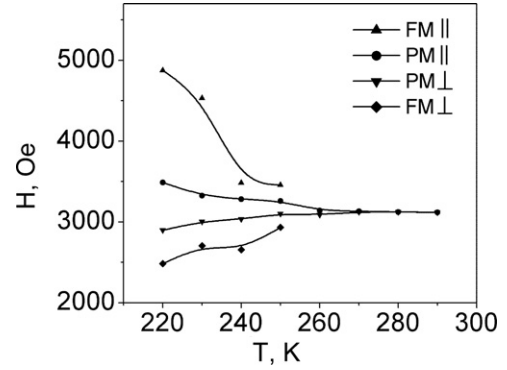
field are transformed in the following:

- if the external magnetic field is parallel to the film plane, then $N_i = 0$ and the resonance field will diminish in the process of FM cluster formation:

$$H_{\mathrm{r1}}^{\parallel} \approx H_w - \frac{4\pi}{3} M_0 f; \tag{11}$$

- if the external magnetic field is perpendicular to the film plane, then $N_i = 1$ and the resonance field will grow in the process of FM cluster formation:

$$H_{\mathrm{r1}}^{\perp} \approx H_w + \frac{8\pi}{3} M_0 f. \tag{12}$$

It is seen that equations (11) and (12) adequately reflect the tendencies obtained in the experiment. What is more, it follows from these expressions that, with the temperature decreasing, the difference $H_{\mathrm{r1}}^{\perp} - H_w$ should grow more rapidly than the difference $H_{\mathrm{r1}}^{\parallel} - H_w$, and this is actually observed in experiment (see figures 5 and 6).

At this stage, it is pertinent to note that the films of sodium-doped manganites are especially suitable for the experiments aimed at the comprehension of the interference of coexisting magnetic phases. By means of the variation of the heat treatment mode, it is possible to affect in different ways the features of the temperature evolution of FM and PM phases. On the one hand, the heat treatment gives rise to the changes in the relative amount of amorphous/crystalline phase in the samples. On the other hand, due to the enhanced volatility of sodium at high temperatures, it can be used to tune the temperature range of the magnetic phase coexistence. Thus, the change in the film composition or heat treatment modes is expected to result in the change of the temperature of the FM phase nucleation and the width of the magnetic transition, with the main regularities of the phase interference being kept unchanged.

4. Conclusions

The features of the temperature evolution of the ESR spectra have been studied for the partially crystallized

La$_{0.84}$Na$_{0.16}$MnO$_3$ films, where the PM and FM phases coexist over a wide temperature range. It is shown that the presence of the FM phase changes the resonance conditions for the PM phase, which has usually been neglected while studying complex systems of such a kind. The effect is successfully explained with the use of a simple model which takes into account the magnetodipole contribution from the FM clusters to the magnetic field acting on the PM phase. It is demonstrated that the resonance field of the PM phase becomes dependent on the shape of the sample, the saturation magnetization and the fraction of the FM phase. As a result, the effect is strongly dependent on the orientation of the external magnetic field with respect to the film plane, which well agrees with the results of the experiment. It is shown that the features of the effect observed can be varied by means of the variation of the fabrication conditions.

Acknowledgments

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