Indian J. Phys. **75A (4), 313-316 (2001)**

IJP A
an international journal

Electron magnetic resonance in doped colossal magnetoresistive manganites

A I Shames, E Rozenberg* and G Gorodetsky
Department of Physics, Ben-Gurion University of the Negev POB 653, 84105,
Beer-Sheva, Israel

W H McCarroll
Chemistry Department, Rider University, 2083 Lawrenceville Road,
Lawrenceville, NJ 08854, USA

and

M Greenblatt
Department of Chemistry, Rutgers University, Piscataway,
New Jersey 08854-8087, USA

E-mail evgenyr@bgumail.bgu.ac.il

Abstract The experimental results of electron magnetic resonance study on powdered ceramics samples of LaMn-perovskites doped by divalent Pb, Sn and Zn ions, as well as those for powdered single crystals doped by Na are presented. The main and common features observed for the resonant spectra of all the samples could be noted : a) gradual change of the broad asymmetric line of ferromagnetic resonance (FMR) to narrow line of electron paramagnetic resonance (EPR) with temperature T; b) coexistence within certain temperature intervals of FMR and EPR signals, as well as the signals of FMR and ferromagnetic antiresonance ; c) minimum of the linewidth in the vicinity of 1.1 T_c and its linear broadening above this temperature; d) double integrated intensity of the signal obeys Arrhenius law above 1.1 T_c ; e) specific effect of the non-resonant surface microwave absorption. The results obtained for poly- and single-crystalline samples are compared. The disputable problems in this field are noted.

Keywords : Ferromagnetic resonance, electron paramagnetic resonance, Mixed-valence doped manganites

PACS Nos. : 76.50.+g, 76.30 Fc

1. Introduction

The perovskite manganites of the form $(La_{1-x}A_x)MoO_3$, where A is a divalent ion such as Ca, Sr, Ba etc., have become recently a fascinating system for researchers due to variety of their magnetic and conductive properties[1-4]. The undoped stoichiometric (x = 0) $LaMnO_3$ contains only Mn^{3+} ions and is classified as canted antiferromagnet (AF). The substitution of La^{3+} by divalent A^{2+} ions results in a mixed valency of Mn^{3+} and Mn^{4+} ions and a variety of electronic and magnetic phases. The ferromagnetic (FM) ordering is governed mostly by a double-exchange (DE) interaction Mn^{3+}–O^{2-} – Mn^{4+}. In most A^{2+} doped manganites, a transition from a metallic FM to a paramagnetic semiconductor-like phase occurs at a temperature T_m, upon heating. This transition manifests itself by a maximum $\rho_m(T)$ in the resistivity. A special attention is addressed to "colossal magnetoresistance" (CMR) effect in these compounds, being a huge (up to thousandfold) change in resistivity under an external magnetic field, in the vicinity of the Curie point T_c.

Electron magnetic resonance (EMR), namely, electron paramagnetic resonance (EPR) at $T > T_c$ and ferromagnetic resonance (FMR) at $T < T_c$, is a useful tool for studying a magnetic structure and its change under the influence of external parameters (magnetic field H, temperature T, etc.). The use of EMR technique for studying the perovskite manganites starts from 1969[5] and is intensively developed during last years (see for example [3,6,7] and references therein). The current paper presents the brief review of the recent results of EMR studies of doped La-perovskite manganites obtained in the Laboratory of Magnetic Resonance of Ben-Gurion University of the Negev. The results, presented in the Section 2, are focused on studies of Pb, Sn and Zn-doped polycrystalline LaMn-perovskites. Section 3 contains data on EMR properties of grounded (powdered) single-crystalline $La_{0.887}Na_{0.113}Mn_{0.984}O_3$ samples. Discussion and conclusions are in Section 4.

---

[*] Corresponding Author

2. Experimental details and results

EMR measurements on powder samples in the temperature range 100 (± 0.5) $\leq T \leq$ 420 (± 0.5) K were carried out using Bruker EMX-220 digital X-band (9.40 GHz) spectrometer and ER 4121 VT temperature controller (for Zn- and Na-doped samples the above interval was extended down to 4.2 K). The processing of the spectra was performed by Bruker WIN-EPR Software. In order to eliminate size effects and cavity overloading, powder samples of several mg were placed at the bottom of 1-mm glass capillary tubes centered in the rectangular cavity. The measurements were done in the linear response regime at microwave power 200 μW. In contrast to the results obtained by Seehra *et al* [8], no asymmetric (Dysonian-like) line-shapes were observed in the paramagnetic region, which allowed us to work without any dilution of samples.

The polycrystalline Pb, Sn and Zn-doped manganites were obtained by standard ceramic technology (see, for instance, [9]). The Curie temperatures for $La_{1-x}Zn_xMnO_3$ samples, obtained by susceptibility measurements, were found as T_c = 180 K; 160 K; 150 K and 125 K (within the experimental error of ± 2K) for x = 0.05; 0.1; 0.2 and 0.3 correspondingly. The procedure of growth of single-crystalline samples of $La_{0.887}Na_{0.113}Mn_{0.984}O_3$ by fused-salt electrolysis is presented in [10], T_c was found to be 300 K.

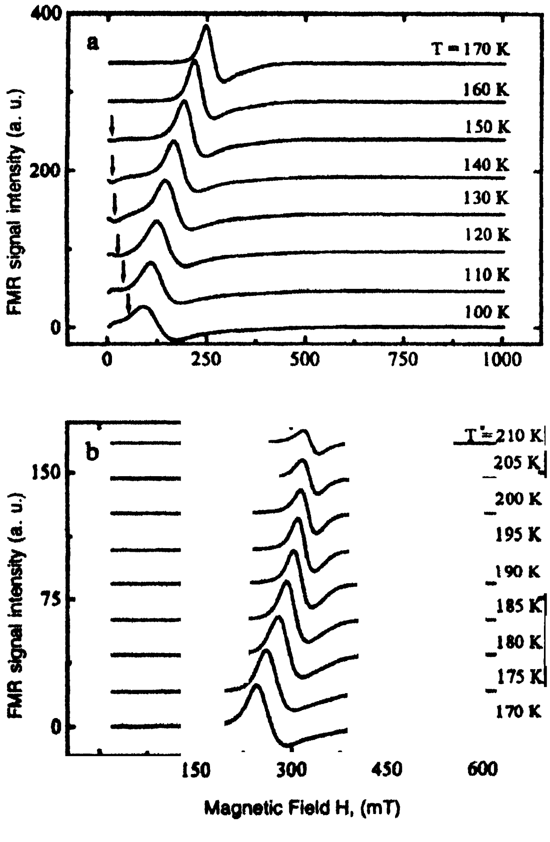

Figure 1. Temperature dependence of EMR spectra of polycrystalline $La_{0.95}Zn_{0.05}MnO_3$: (a) below Curie temperature T_c =180 K, vertical arrows point the position of ferromagnetic antiresonance signal ; (b) close to and above T_c.

The following main and common features of EMR spectra (the typical graphs are presented for Zn-doped powdered manganites) were observed in polycrystalline samples [9,11].

(i) A typical asymmetric broad FMR single exists at $T < T_c$. It changes gradually, *i.e.*, narrows and shifts to higher H when the external temperature increases. At approaching T_c the FMR signal gradually turns to the symmetric Lorentzian EPR signal which is observed at $T \geq 1.1\ T_c$ (Figure 1). The g-factor within the paramagnetic region decreases from the values above 2.0 to 1.987 ± 0.001, which is close to that of non-coupled Mn^{4+} ions.

(ii) The ferromagnetic antiresonance (FAR) is observed within some interval of temperatures at $T < T_c$. It manifests itself as a low-field dip in the FMR spectra. The unusual (not described by theory used in [12]) temperature dependence of the resonant field of FAR, *e.g.* its shift towards zero field when the temperature approaches T_c, is observed (Figure 1a, vertical arrows).

(iii) Within certain interval of temperatures $T < 1.1\ T_c$ a narrow EPR signal coexists with a broad FMR one. The above signals may be superimposed one on another or notably shifted on H depending on the nature of doping ion, as well as on crystal structure of the sample (single-or polycrystalline one).

(iv) The linewidth (ΔH_{pp}) of the EMR signal has a pronounced minimum in the vicinity of $T \approx 1.1 T_3$. At the temperatures above 1.1T_c and up to at least 2T_c, the EPR line broadens linearly (figure 2).

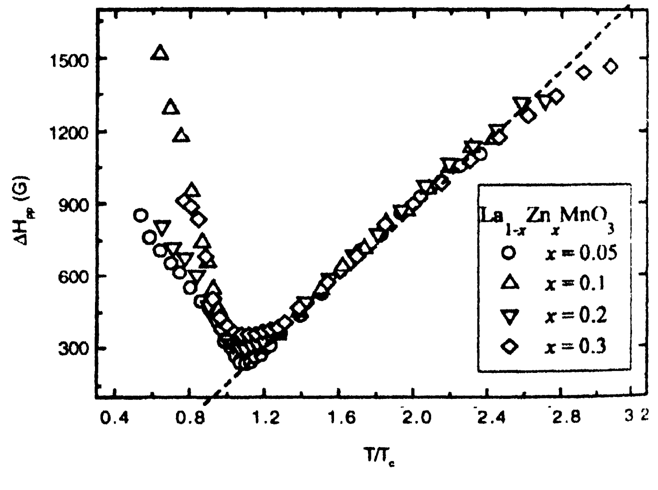

Figure 2. Dependence of the EMR linewidth ΔH_{pp} for polycrystalline $La_{1-x}Zn_xMnO_3$ samples *vs.* normalized temperature. The straight line describes a linear fit (the same for all samples) at $T > 1.1\ T_c$.

(v) The normalized double integrated intensity (DI) of the EPR signals (Figure 3a) are well fitted at $T > 1.1\ T_c$ by an Arrhenius relation of the form [13] :

$$DI = I_0 \exp(\Delta K / k_B T), \qquad (1)$$

where' ΔE in interpreted as a thermal activation energy for dissociation of spin clusters (Figure 3b).

(vi) The effect of non-resonant surface microwave absorption first observed on manganites by Lofland *et al* [6] for $H \parallel E$, was detected for the geometry $H \perp E$ typical in magnetic resonance experiments. This effect manifests itself by the non-trivial temperature dependence of double integrated resonance signal, having a maximum at $T < T_c$ (see, for example Ref. [9] and Figure 3a).

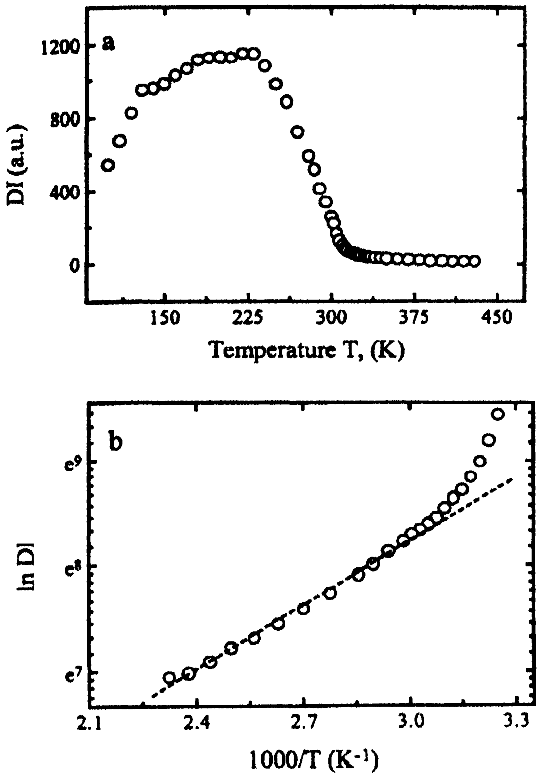

Figure 3. Temperature dependence of the intensity of EMR signal for polycrystalline $La_{0.887}Na_{0.113}Mn_{0.984}O_3$ sample : (a) normalized double integrated intensity (DI) of the first derivative signal ; (b) Arrhenius plot of DI at temperature above T_c.

3. Results for single-crystalline powders

The great advantage of ground single-crystals as an object for EMR study is their chemical "single-phase" state giving possibility for manifestation of additional details on investigated spectra. At the same time, all the above peculiarities of the spectra are the intrinsic ones, characteristic for investigated manganites. This suggestion is directly confirmed by experimental data, obtained on powdered single-crystalline samples of $La_{0.887}Na_{0.113}Mn_{0.984}O_3$.

All the regularities (i) – (vi) described in Section 2 are also characteristics for EMR spectra of these samples. Additionally, the temperature interval of the coexistence of FMR and EPR signals (regularity (iii)) is extended up to $\Delta T \approx 70\,K$. The lines are clearly separated (Figure 4a). The next important feature of observed spectra is the presence of noise-like oscillations on FMR line, while the EPR signal of about the same intensity is a noiseless one. This feature may be better observed in the 2-nd derivative spectrum at the same temperature (Figure 4b). It is important to note that the FMR spectra of the bulk single-crystals consist of superposition of multiple sharp lines, which are both orientational- and temperature-dependent at $T < 1.1\,T_c$ (Figures 4c, d). To our mind, the above noted oscillations result from such structure the spectra of bulk single-crystals.

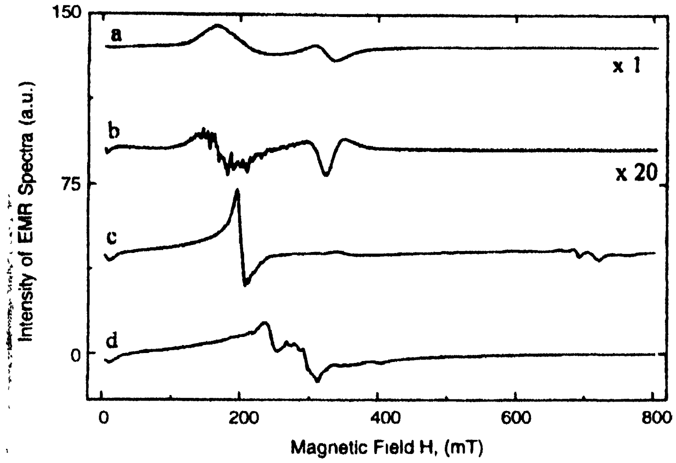

Figure 4. EMR spectra of $La_{0.887}Na_{0.113}Mn_{0.984}O_3$ samples at $T = 290$ K : (a) first derivative EMR spectrum of polycrystalline sample , (b) second derivative EMR spectrum of polycrystalline sample at higher receiver gain ; (c) first derivative EMR spectrum of single-crystalline sample, H ||<001>, (d) first derivative EMR spectrum of single-crystalline sample, H ||<010>

4. Discussion and conclusions

The main result of our EMR investigation is the presence of intrinsic magnetic inhomogeneities in all of the manganites under consideration. At $T > T_c$ inhomogeneities (various magnetically ordered subsystems) manifest itself as short-range FM ordered entities dissociating with T according to the Arrhenius Law eq. (1). Moreover, magnetic inhomogeneities are clearly detected at $T < T_c$ (see, for example, Figure 4), where paramagnetic "domains" exist within FM matrix and contribute a notable EPR signal to the resultant spectra. The last observation is strongly confirmed by NMR and EMR data of [13-16].

Surprisingly, the magnetic inhomogeneities are (in some way) more pronounced in single-crystalline samples. It results in the extended temperature interval of the coexistence of EPR and FMR signals. On the other hand, very complex structure of FMR spectra of bulk single-crystalline sample (and noise-like oscillations on spectra of powders) noted in Section 3 may also be connected with aforenamed inhomogeneities. Namely, the volume of the bulk crystal may contain a number of regions with different constants of magnetocrystalline anisotropy, T_c's *etc.*, connected with local structural defects or non-stoichiometry. Up to now, the data on resonant properties of single-crystalline manganites are not numerous, but FMR spectrum of Pb-doped sample presented in Ref. [12] clearly shows a complicated structure similar to that noted in this paper. Investigations of EMR properties of single crystals are now in progress and the results will be published elsewhere.

Measurements of resonant properties of single crystals directly confirm also our interpretation of the effect of non-resonant surface microwave absorption (regularity (vi) in Section

2). Namely, the above effect (maximum in the temperature dependence of DI) is absent for the bulk samples with strongly reduced area of interfaces. The model of one phonon spin-lattice relaxation process [8] may explain the linear broadening of the linewidth (regularity (iv)) at paramagnetic temperatures. The minimum linewidth found at T ~ 1.1 T_c may be associated with exchange narrowing as a consequence of enhanced double exchange within the cluster due to high localization of the wave function of the change carriers [11]. At the same time, the reason for equal (within the experimental error) slope of linear dependence of ΔH_{pp} vs. normalized temperature T/T_c (see Figure 2) observed for numerous different manganites at $T > 1.1\ T_c$ is not understood at the moment. The absence of the theoretical interpretation of the "universal" 1.1 T_c value could also be noted.

Acknowledgments

The research was supported by the Israeli Science Foundation administered by the Israel Academy of Sciences and Humanities and the Israeli Ministry of Immigrant Absorption for the CAMEO fellowship (A. Sh. and E. R.). Authors thank Dr. B. Revzin for sintering of Zn-doped samples.

References

[1] A P Ramirez *J. Phys. : Cond Matter.* **9** 8171 (1997)

[2] *Colossal Magnetoresistance Charge Ordering and Related Properties of Manganese Oxides* (ed) C N R Rao and B Raveau (Singapore ; World Scientific) p 345 (1998)

[3] J M D Coey, M Viret and S von Molnar *Adv Phys.* **48** 167 (1999)

[4] A J Millis *Nature* **392** 147 (1998)

[5] C W Cearle and S T Wang *Canad J. Phys.* **47** 2703 (1969)

[6] S E Lofland, P H Kim, P Dahiroct, S M Bhagat, S D Tyagi, C Kwon, R Shreekala, R Ramesh and T Venkatesan *J. Phys Cond Matter* **9** 6697 (1997)

[7] M T Causa, M Tovar, A Caneiro, F Prado, G Ibanez, C A Ramos, A Butera, B Alascio, X Obrados, S Pinol, F Rivadulla, C Vazquez Vazquez, M A Lopez- Quintela, J Rivas, Y Tokura and S B Oseroff *Phys Rev.* **58B** 3233 (1998)

[8] M S Seehra, M M Ibrahim, V Suresh Babu and S Srinivasan *J Phys : Cond. Matter* **8** 11283 (1996)

[9] A I Shames, E Rozenberg, G Gorodetsky, J Pelleg and B K Chaudhuri *Solid State Commun.* **107** 91 (1998)

[10] W H McCarroll, Ian D Fawcett, M Greenblatt and K V Ramanujachary *J Solid State Chem.* **146** 88 (1999)

[11] A I Shames, E Rozenberg, G Gorodetsky, B Revzin, D Mogilyanski J Pelleg and I Felner *JMMM* **203** 259 (1999)

[12] C A Ramos, M T Causa, M Tovar, X Obrados and S Pinol *Ibid* **177-181** 867 (1998)

[13] S B Oseroff, M Torikachvili, J Singley, S Ali, S-W Cheong and S Schultz *Phys. Rev* **B53** 6521 (1996)

[14] G Papavassiliou, M Fardis, F Milia, A Simopoloulos, G Kallias, M Pissas, D Niarchos, N Ioannidis, C Dimitropoulos and J Dolinsek *Phys Rev* **B55** 15000 (1997)

[15] Cz Capusta, P C Riedi, W Kochemba, C J Tomka, M R Ibarra, J M De Teresa, M Viret and J M D Coey *J Phys Cond Matter* **11** 4097 (1999)

[16] J -P Renard and A Anane *Mater Science Engg* **B63** 22 (199