

# Abrupt Changes in the Temperature Dependence of the ESR Linewidth of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ Single Crystals

I. V. Yatsyk<sup>a</sup>, R. M. Eremina<sup>a</sup>, M. M. Shakirzyanov<sup>a</sup>, Ya. M. Mukovskii<sup>b</sup>,  
H.-A. Krug von Nidda<sup>c</sup>, and A. Loidl<sup>c</sup>

<sup>a</sup> *Zavoiskii Physicotechnical Institute, Kazan Scientific Center, Russian Academy of Sciences, Sibirskii trakt 10/7, Kazan 29, 420029 Russia*  
e-mail: I.Yatzyk@gmail.com

<sup>b</sup> *Moscow Institute of Steel and Alloys, Leninskii pr. 4, Moscow, 119049 Russia*

<sup>c</sup> *Experimentalphysik V, Elektronische Korrelationen und Magnetismus, Universität Augsburg, 86135 Augsburg, Germany*

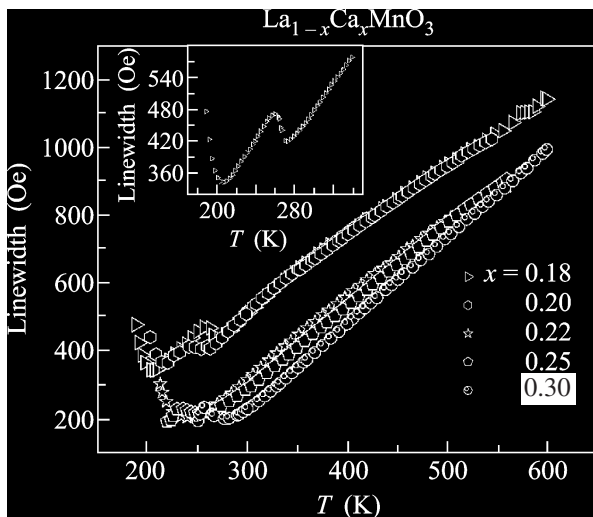
The temperature dependence of the ESR linewidth in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  single crystals with various dopant concentrations ( $x = 0.18, 0.2, 0.22, 0.25,$  and  $0.3$ ) has been studied. An abrupt decrease in the ESR linewidth has been observed in the samples with a dopant concentration of  $x = 0.18$  and  $0.2$  near the respective temperatures  $T_{OO'} \approx 260$  and  $240$  K of the orthorhombic to pseudocubic structural phase transition. The abrupt decrease in the ESR linewidth by approximately 180 Oe has been also observed in the whole temperature range when the concentration is increased from  $x = 0.2$  to  $x = 0.22$ . The formula for the fourth moment of the ESR line has been derived including both crystal fields and isotropic exchange interactions and taking into account the difference between the exchange coupling of a spin to its nearest in-plane and out-of-plane neighbors. The formula has been used to estimate the parameter  $D$  of the crystalline field on  $\text{Mn}^{3+}$  ions.

The intensive study of the physical properties of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $\text{Me} = \text{Ca}, \text{Ba}, \text{Sr}$ ) manganites is stimulated by the variety of their properties as well as by the phenomenon of colossal magnetoresistance. The parent compound  $\text{LaMnO}_3$  is an antiferromagnet, where all manganese ions are in the trivalent  $\text{Mn}^{3+}$  ( $3d^4$ ) state with the spin  $S = 2$ . Doping of  $\text{LaMnO}_3$  with a divalent metal ( $\text{Me} = \text{Ca}, \text{Ba}, \text{Sr}$ ) changes the valence state of some manganese ions to  $\text{Mn}^{4+}$  ( $3d^3$ ) with the spin  $S = 3/2$ . Moreover, as mentioned by Nagaev [1], the holes at low doping levels are distributed over the oxygen sites and the valence of the manganese ions does not change. Thus, at different dopant concentrations, the ground state may be a canted antiferromagnet, a ferromagnetic insulator, or a metal. The resulting phase diagram of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  manganites is extremely rich [2, 3].

Electron spin resonance (ESR) in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  manganites was studied in a number of works [4–9] and the general features of the spectra are well described. At the same time, some important peculiarities were set aside. This concerns, in particular, the spectra of single crystals with a doping level  $x$  that corresponds to the phase boundaries. For example, a transition from a ferromagnetic insulator to a ferromagnetic metallic state occurs at a calcium concentration of  $x \approx 0.22$ . In the

vicinity of  $x = 0.2$ , the magnetic and transport properties of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  are especially sensitive to small variations in the calcium and oxygen concentrations [10]. An orthorhombic to pseudocubic structural phase transition is observed in the paramagnetic region of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  with a calcium concentration below 20%. The transition temperature decreases with an increase in concentration from 760 K at  $x = 0$  to  $\approx 240$  K at  $x = 0.2$ . Further study is required to understand the nature of these important changes.

Single crystals of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  with  $x = 0.18, 0.2, 0.22, 0.25, 0.3$  and of  $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$  were grown by means of zone melting with radiative heating [11]. The disks of a diameter of 3 mm and a height of about 0.2 mm were prepared for ESR experiments. The plane of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  disks with  $x = 0.2, 0.22, 0.25,$  and  $0.3$  was normal to the [110] direction. The plane of the  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  single-crystal disk coincided with the ( $ac$ ) plane. The ESR spectra were measured on Bruker and Varian X-band spectrometers at temperatures ranging from 200 to 600 K. The ESR spectra of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x = 0.18, 0.2, 0.22, 0.25,$  and  $0.3$ ) and  $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$  single crystals exhibit one line with an effective  $g$  factor of approximately 2. The ESR line-shape strongly depends on the temperature near the ferromagnetic-to-paramagnetic phase transition. Shames



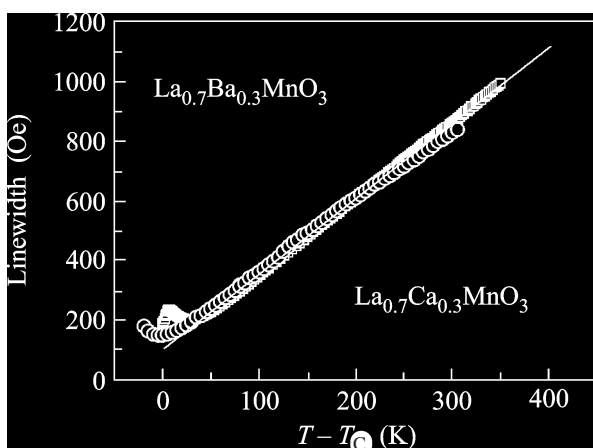
**Fig. 1.** Temperature dependence of the ESR linewidth in the  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  single crystals. The inset magnifies an abrupt change in the linewidth of  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  single crystal near a temperature of  $T \approx 260$  K.

et al. [7] pointed out that the ESR signal has a Lorentzian shape for the samples with  $x = 0.18, 0.2$  and  $x = 0.22$  starting from  $T = 220$  and  $230$  K, respectively. One Lorentzian line was observed in the ESR spectrum at temperatures much above  $T_C$ . The temperature dependence of the ESR linewidth for  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x = 0.18, 0.2, 0.22, 0.25,$  and  $0.3$ ) single crystals is shown in Fig. 1. The linewidth increases with the temperature for all samples studied in this work. At the same time, the ESR linewidth of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  ( $x = 0.18, 0.2$ ) single crystals exhibits an anomalous abrupt decrease near  $T \approx 260$  K and  $T \approx 240$  K, respectively (see the inset in Fig. 1). According to Boitteau et al. [2] and Pis-

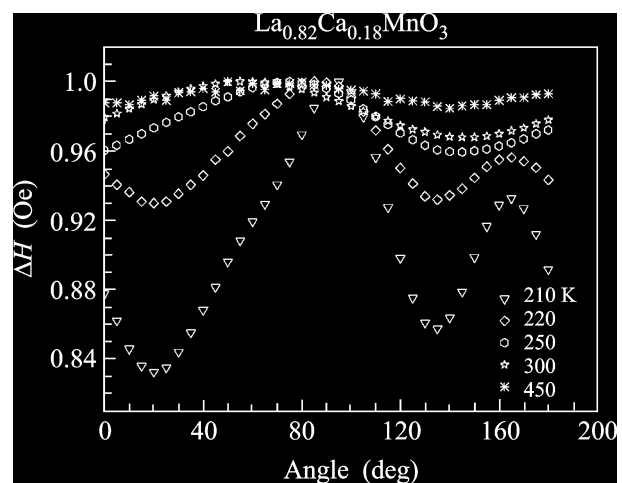
sas [3], structural transitions from the orthorhombic  $O'$  phase to the pseudocubic  $O$  phase occur in these crystals at the above temperatures. As seen from Fig. 1, the ESR linewidth of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  with  $x = 0.18$  and  $0.2$  at the same temperature decreases insignificantly. An abrupt decrease in the ESR linewidth with a change in the calcium concentration from  $x = 0.2$  to  $x = 0.22$  is remarkable. The linewidth decreases insignificantly with the further increase in the concentration from  $x = 0.22$  to  $x = 0.25$  and  $0.3$ . The difference in the ESR linewidth between the concentrations  $x = 0.2$  and  $x = 0.22$  is  $180\text{--}190$  Oe for all temperatures. It is  $70\%$  of the ESR linewidth of  $\text{La}_{0.78}\text{Ca}_{0.22}\text{MnO}_3$  at  $T \approx 280$  K. This is most probably attributed to a change in the sample conductance with a change in the concentration of calcium ions in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  with  $x$  varying from  $0.2$  to  $0.22$ , since the manganite with  $x = 0.2$  and  $0.22$  is a ferromagnetic insulator and a ferromagnetic metal, respectively.

No specificity was noticed in the temperature dependence of the ESR linewidth of  $\text{La}_{0.7}\text{Me}_{0.3}\text{MnO}_3$  ( $\text{Me} = \text{Ca}, \text{Ba}$ ) single crystals with a doping of  $x = 30\%$ , except for a general increase with the temperature (Fig. 2). The horizontal axis is  $T - T_C$ , where  $T_C$  is the temperature of the ferromagnetic-to-paramagnetic phase transition. Obviously, the temperature curves are almost linear and coincide for both substances.

The angular dependence of the ESR linewidth of  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  single crystals in the  $(ac)$  plane was also studied at different temperatures (Fig. 3). According to the data, the ESR linewidth anisotropy decreases with an increase in the temperature. The anisotropy is  $15\%$  at  $T = 210$  K, while the ESR linewidth at  $T = 450$  K almost does not change and the anisotropy in the  $(ac)$  plane is  $\sim 2\%$ . Any angular anisotropy of the ESR



**Fig. 2.** Temperature dependence of the ESR linewidth in the  $\text{La}_{0.7}\text{Me}_{0.3}\text{MnO}_3$  ( $\text{Me} = \text{Ca}, \text{Ba}$ ) single crystal. The horizontal axis is  $T - T_C$ , where  $T_C$  is the temperature of the ferromagnetic-to-paramagnetic phase transition.



**Fig. 3.** Angular dependence of the ESR linewidth in the  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  single crystal relative to the maximum value at each temperature.

spectrum was not observed in  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  with a calcium doping level of  $x = 0.22, 0.25,$  and  $0.3$ .

At the same time, the angular and temperature dependence of the  $g$  factor of  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  was studied. The position of the ESR line is almost independent of the direction of the magnetic field within the ( $ac$ ) plane. The temperature dependence of the  $g$  factor along the  $b$  axis of  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  is shown in Fig. 4. The  $g$  factor decreases with the temperature increase. A peak is seen near 260 K, which corresponds to the  $O-O$  orthorhombic-to-pseudocubic phase transition [2].

The observation of ESR in manganites is known to be due to the exchange narrowing effect. The isotropic exchange interaction of manganese ions results in the Lorentzian shape of the ESR line, whose linewidth may be described by the combination of the second,  $M_2$ , and fourth,  $M_4$ , moments [12]:

$$\Delta H = \pi \sqrt{M_2^3/3M_4}. \quad (1)$$

The spin interaction Hamiltonian has the form

$$H = H_{\text{ex}} + H_{\text{cr}} + H_{\text{an}}, \quad (2)$$

where

$$H_{\text{ex}} = \sum_{i=1}^4 J_{\text{ac}} S_0 S_i + \sum_{i=5}^6 J_b S_0 S_i$$

is the superexchange interaction of the manganese-ion spin  $S_0$  with its nearest in-plane ( $ac$ ) and out-of-plane neighbors;  $H_{\text{cr}} = DS_z^2 + E(S_x^2 - S_y^2)$  is the spin Hamiltonian of the crystal field in the local coordinate system of the octahedron (in the coordinate system with the  $z'$  axis directed along the external magnetic field, the crystal field Hamiltonian may be expressed as  $H_{\text{cr}} = \sum_{i,j=x',y',z'} \lambda_{ij} S_i S_j$ , where the functions  $\lambda_{ij}$  of the rotation angles and of the parameters  $D$  and  $E$  are given in the Appendix); and  $H_{\text{an}} = \sum_{\zeta,\xi=x,y,z}^6 J_{\zeta\xi} S_0^{\zeta} S_i^{\xi}$  is the

Hamiltonian of anisotropic symmetric and antisymmetric interactions. As pointed out in [13], the dominant contribution to the linewidth in the orthorhombic phase is due to the effects of the crystal field. Our measurements of the angular dependence of the ESR linewidth presented in Fig. 3 support this hypothesis. The oscillation amplitude of the ESR linewidth decreases with the temperature increase and the oscillations almost disappear under the transition to the pseudocubic phase; this behavior is naturally attributed to the vanishing of the parameters  $D$  and  $E$ . A complete theory of the ESR linewidth in such complicated systems as manganites has not yet been developed. However, the method of calculating the moments of the line in the high-temperature approximation is known [12] and we use it. The expression for the second moment of the line is known in the

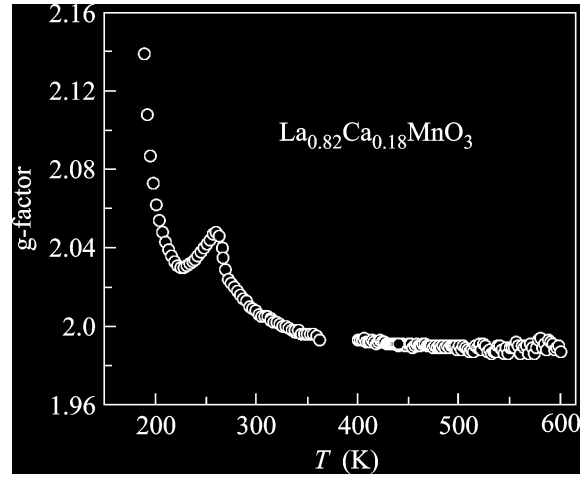


Fig. 4. Temperature dependence of the  $g$  factor in the  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  single crystal. The magnetic field is directed along the  $b$  axis.

coordinate system where the  $z'$  axis is parallel to the external magnetic field [14]

$$M_2 = \frac{1}{20h^2} (4a - 3) C_{xyz}, \quad (3)$$

where

$$C_{xyz} = (\lambda_{xx} - \lambda_{yy})^2 + 4\lambda_{xy}^2 + 10(\lambda_{xz}^2 + \lambda_{yz}^2) + (\lambda_{xx} + \lambda_{yy} - 2\lambda_{zz})^2,$$

$a = S(S + 1)$ , and  $h$  is Planck's constant. The primes are omitted in Eqs. (3) and (4) for brevity. The expression for the fourth moment taking into account the isotropic exchange interaction and crystal field is obtained in this work and reads as

$$M_4 = (4J_{\text{ac}}^2 + 2J_b^2) \frac{a}{10h^4} (4a - 3) C_{xyz}, \quad (4)$$

where  $J_{\text{ac}}$  and  $J_b$  are the parameters of the isotropic exchange interaction between the spins of manganese ions in the ( $ac$ ) plane and along the  $b$  axis, respectively.

At an intermediate doping level, the valence of a part of manganese ions changes from  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$ . We assume that the four-valent Mn ions are evenly distributed in the sample. Then,  $\text{Mn}^{4+}$  may be one of the four in-plane neighbors of  $\text{Mn}^{3+}$ , occupying the central position or the position  $\text{Mn}^{3+}$  in one of the two neighboring planes. This results in a change in the magnitude of the isotropic exchange interaction between the manganese spins. The crystal fields are different for  $\text{Mn}^{3+}$  and  $\text{Mn}^{4+}$ . Obviously,  $D(\text{Mn}^{3+})$  in the orthorhombic phase is much higher than  $D(\text{Mn}^{4+})$  in the pseudocubic symmetry. Since  $\text{CaMnO}_3$  has pseudocubic symmetry [4], the manganese ions are only in the four-valent state in this compound. Based on these considerations, the abrupt

decrease in the ESR linewidth in  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  can be attributed to a change in the crystal field on the  $\text{Mn}^{3+}$  ion.

We use the parameters of the isotropic exchange interaction according to the neutron scattering data [15] and estimate the magnitude of the crystal field from the experimental ESR linewidth. When calculating the contribution of the single-ion anisotropy to the ESR linewidth, one has to take into account that there are four nonequivalent positions of manganese ions in the crystal lattice of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  [16]. Each manganese ion is surrounded by six oxygen ions that form an octahedron. We choose the local coordinate system of the octahedron in the following way: the  $z$  axis is directed along the Mn–O1 bond, the  $x$  and  $y$  axes lie in the basal plane and are directed along the lines drawn from Mn to the center of O2(2)–O2(3) and O2(1)–O2(2) bonds, respectively. We assume that the components of the  $g$  tensor coincide with those of the crystal field in such a local coordinate system of the octahedron. The values of the direction cosines of the local coordinate system with respect to the crystallographic axes are given in the Appendix for four magnetically nonequivalent positions of manganese ions in the octahedron. The lattice parameters of  $x = 0.18$  single crystals are  $a = 5.5062 \text{ \AA}$ ,  $b = 7.7774 \text{ \AA}$ , and  $c = 5.514 \text{ \AA}$ ; the lattice is orthorhombic with the perovskite structure [16]. The isotropic exchange interaction constants  $J_{ac}$  and  $J_b$  were obtained by Hennion et al. [15] with the use of inelastic neutron scattering on  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$ . The exchange interactions are of a ferromagnetic character,  $J_{ac} = 2.5 \text{ meV}$  within the  $ac$  plane and  $J_b = 1.2 \text{ meV}$  between the planes. Using these values, we find that the drop in the ESR linewidth of  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  corresponds to 50 Oe for  $D = 0.79 \text{ K}$  and  $E = 0 \text{ K}$ . This  $D$  value seems quite reasonable, thus indicating the correctness of the microscopic model of the origin of the drop in the ESR linewidth.

Let us now discuss the abrupt change in the ESR linewidth of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  at the concentration of calcium ions changing from  $x = 0.2$  to  $x = 0.22$ . At a temperature of 300 K, the ESR linewidth of  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$  and  $\text{La}_{0.78}\text{Ca}_{0.22}\text{MnO}_3$  is 492 and 309 Oe, respectively. As seen from Fig. 1, this difference in the ESR linewidth of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  with  $x = 0.2$  and  $x = 0.22$  is almost independent of the temperature. One may suppose that the magnitude of the isotropic exchange interaction changes considerably with an increase in the calcium concentration, which results in a decrease in the ESR linewidth. The direct data on the magnitude of the isotropic exchange interaction in  $\text{La}_{0.78}\text{Ca}_{0.22}\text{MnO}_3$  are absent in the literature, but the Curie temperature  $T_C$  is known to be  $180 \pm 1$ ,  $183.5 \pm 1$ ,  $189.3 \pm 1$ , and  $240 \pm 1 \text{ K}$  for  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$ ,  $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ ,  $\text{La}_{0.78}\text{Ca}_{0.22}\text{MnO}_3$ , and  $\text{La}_{0.75}\text{Ca}_{0.25}\text{MnO}_3$ , respectively [17]. The Curie temperatures of the  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  compounds with  $x = 0.18$ ,

0.2, and 0.22 are almost the same and the magnitude of the isotropic exchange interaction may be expected to also remain unchanged. The strong decrease in the ESR linewidth under the variation in the calcium concentration is naturally associated with the fact that  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  becomes conductive at  $x > 0.2$ . The valence state of some manganese ions is changed from  $\text{Mn}^{3+}$  to  $\text{Mn}^{4+}$  and the state  $\text{Mn}^{4+}$  is smeared over the crystal.

We also performed a comparative study of the temperature dependence of the ESR linewidth in the  $\text{La}_{0.7}\text{Me}_{0.3}\text{MnO}_3$  ( $\text{Me} = \text{Ca}, \text{Ba}$ ) manganites. Figure 2 presents the temperature dependence of the ESR linewidth for two single-crystal manganites, one doped with 30% Ba and the other one with 30% Ca. The horizontal axis is marked in units of  $(T - T_C)$ , where  $T_C = 250$  and  $340 \text{ K}$  for  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  and  $\text{La}_{0.7}\text{Ba}_{0.3}\text{MnO}_3$ , respectively. As seen in the figure, the temperature behavior of the ESR linewidth is almost the same for the two samples and may be described by the linear dependence  $\Delta H = \Delta H_0 + b(T - T_C)$ . We may assume that the contribution linear in temperature to the ESR linewidth of manganites doped with 30% bivalent ions is associated with the interaction of the localized moments of manganese ions with the spins of the charge carriers. It follows from our experimental dependence that  $b = 2.5 \text{ Oe/K}$ .

In conclusion, the ESR study of  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  single crystals with  $x = 0.18, 0.2, 0.22, 0.25,$  and  $0.3$  has been carried out. It has been found that the ESR linewidth decreases sharply (by 180–190 Oe) under the concentration change of calcium ions from  $x = 0.2$  (ferromagnetic insulator) to  $x = 0.22$  (ferromagnetic metal). An abrupt decrease (by 50 Oe) has been observed in the temperature dependence of the ESR linewidth of  $\text{La}_{0.82}\text{Ca}_{0.18}\text{MnO}_3$  near the temperature of the orthorhombic-to-pseudocubic structural phase transition. A microscopic model of the observed phenomenon has been proposed and numerical estimates have been obtained. The expression for the fourth moment of the ESR line has been derived taking into account the crystal-field effects.

## APPENDIX

The transformation of the Cartesian coordinates from the local coordinate system of an octahedron to the crystallographic coordinate system under the rotation of the axes is described by the transformation matrix  $T$ . The  $g$  tensor in the local coordinate system of the octahedron of oxygen atoms has the diagonal form

$$G_{XYZ} = \begin{bmatrix} g_{xx} & 0 & 0 \\ 0 & g_{yy} & 0 \\ 0 & 0 & g_{zz} \end{bmatrix}.$$

It is transformed to the crystallographic coordinate system according to the formula  $G_{ABC} = T^{-1}G_{XYZ}T$ . In the coordinate system where the  $z'$  axis is directed along the external magnetic field, the  $g$  tensor is equal to  $G_{z'} = G_{ABC}F$ , where  $F = (\sin\theta\cos\varphi \ \sin\theta\sin\varphi \ \cos\theta)$ ,

$$T_{1,4} = \begin{bmatrix} -0.0824 \mp 0.1823 & 0.9798 \\ 0.9964 & 0.0000 & 0.0844 \\ \mp 0.0250 & 0.9840 & \pm 0.1764 \end{bmatrix},$$

$$T_{2,3} = \begin{bmatrix} \mp 0.9964 \mp 0.0000 & \pm 0.0843 \\ \pm 0.0824 \pm 0.1823 & \pm 0.9798 \\ -0.0250 & 0.9840 & -0.1764 \end{bmatrix}.$$

The local axes of the  $g$  tensor coincide with the axes of the crystal field in the octahedron of oxygen ions surrounding the manganese ion. Consequently, the transformation matrix for the parameters of the crystal field from the local coordinate system to the coordinate system associated with the direction of the external magnetic field has the form  $A = G_{z'}T$  and the Hamiltonian of the crystal field is transformed to the form  $H_{cr} = \sum_{i,j=x'y'z'} \lambda_{ij} S_i S_j$ , where  $\lambda_{ij} = EA_{x'i}A_{xj} - EA_{y'i}A_{yj} + DA_{z'i}A_{zj}$ .

We are grateful to M.V. Eremin and G.B. Teitel'baum for fruitful discussions. This work was supported by the Russian Foundation for Basic Research, project no. 06-02-17401, and by the Deutsche Forschungsgemeinschaft within the Collaborative Research Center SFB 484 (Augsburg).

#### REFERENCES

1. E. L. Nagaev, *Usp. Fiz. Nauk* **166**, 833 (1996) [*Phys. Usp.* **39**, 781 (1996)].

2. G. Biotteau, M. Hennion, F. Moussa, et al., *Phys. Rev. B* **64**, 104421 (2001).  
 3. M. Pissas, I. Margiolaki, G. Papavassiliou, et al., *Phys. Rev. B* **72**, 064425 (2005).  
 4. D. L. Huber, G. Alejandro, A. Caneiro, et al., *Phys. Rev. B* **60**, 12155 (1999).  
 5. A. I. Shames, E. Rosenberg, G. Gorodetsky, et al., *Phys. Rev. B* **68**, 174402 (2003).  
 6. A. Shengelaya, Guo-meng Zhao, H. Keller, et al., *Phys. Rev. B* **61**, 5888 (2000).  
 7. A. I. Shames, E. Rozenberg, M. Auslender, et al., *J. Magn. Magn. Mater.* **910**, 290 (2005).  
 8. A. Auslender, A. I. Shames, E. Rozenberg, et al., *IEEE Trans. Magn.* **43**, 3049 (2007).  
 9. V. A. Atsarkin, V. V. Demidov, F. Simon, et al., *J. Magn. Magn. Mater.* **258–259**, 256 (2003).  
 10. R. Laiho, E. Lahderanta, J. Salminen, et al., *Phys. Rev. B* **63**, 094405 (2001).  
 11. D. A. Shulyatev, S. G. Karabashev, et al., *J. Cryst. Growth* **810**, 237 (2002).  
 12. S. A. Altshuler and B. M. Kozyrev, *Electron Paramagnetic Resonance in Compounds of Transition Elements* (Wiley, New York, 1974; Nauka, Moscow, 1972).  
 13. J. Deisenhofer, B. I. Kochelaev, E. Shilova, et al., *Phys. Rev. B* **68**, 214427 (2003).  
 14. J. Deisenhofer, M. V. Eremin, D. V. Zakharov, et al., *Phys. Rev. B* **65**, 104440 (2002).  
 15. M. Hennion, F. Moussa, P. Lehouelleur, et al., *Phys. Rev. Lett.* **94**, 057006 (2005).  
 16. Q. Huang, A. Santoro, J. W. Lynn, et al., *Phys. Rev. B* **55**, 14987 (1996).  
 17. R. I. Zainullina, N. G. Bebenin, V. V. Ustinov, et al., *Phys. Rev. B* **76**, 014408 (2007).

*Translated by A. Safonov*