# Magnetic and electrical properties of $LBaMn_2O_{6-\gamma}$ (L=Pr, Nd, Sm, Eu, Gd, Tb) manganites

S. V. Trukhanov<sup>\*</sup> and I. O. Troyanchuk<sup>†</sup>

Institute of Solids and Semiconductor Physics, NAS, P. Brovka str. 17, 220072 Minsk, Belarus

M. Hervieu

Laboratoire CRISMAT, ISMRA, Université de Caen, 6 Boulevard du Maréchal Juin, 14050 Caen Cedex, France

H. Szymczak

Institute of Physics, PAS, Lotnikov str. 32/46, 02-668 Warsaw, Poland

K. Bärner

IV. Physikalisches Institut der Universität Göttingen, Bunsenstrasse 13-15, D37073 Göttingen, Germany (Received 4 April 2002; revised manuscript received 19 June 2002; published 22 November 2002)

Influence of cation order-disorder phenomena on the crystal structure, magnetic, and electrical transport properties of new CMR perovskites for  $LBaMn_2O_{6-\gamma}$  (L=Pr, Nd, Sm, Eu, Gd, Tb) series has been investigated. For each rare-earth ion three compounds have been synthesized by the topotactic reduction-oxidation method. Structural investigations have shown the oxygen-stoichiometry LBaMn<sub>2</sub>O<sub>6</sub> compound obtained in air to be cubic with disordered  $L^{3+}$  and  $Ba^{2+}$  cations whereas the oxygen-deficient  $LBaMn_2O_5$  is tetragonal with ordered  $L^{3+}$  and  $Ba^{2+}$  and alternate stacking of rare earth and barium containing layers along c. This crystal structure is similar to the YBaCuFeO<sub>5</sub> related one. Another form of oxygen-stoichiometry  $LBaMn_2O_6$  compound obtained by reoxidation of oxygen-deficient  $LBaMn_2O_5$  is also tetragonal and retains the ordering of  $L^{3+}$  and Ba<sup>2+</sup> cations. It is notable that the reoxidized EuBaMn<sub>2</sub>O<sub>6</sub> compound has an orthorhombic unit cell. It is observed that this type of cation ordering leads to considerable increase of transition temperature to paramagnetic state. For example, disordered EuBaMn<sub>2</sub>O<sub>6</sub> compound has magnetic properties similar to spin glass and shows freezing temperature of magnetic moments  $T_f \approx 40$  K while ordered EuBaMn<sub>2</sub>O<sub>6</sub> is an inhomogeneous ferromagnet with Curie point  $T_C \approx 260$  K. Electrical resistivity behavior correlates with magnetization. Below the  $T_c$  the Pr, Nd, Sm based compounds undergo a transition to metallic state and demonstrate a peak of magnetoresistance. It is supposed that the remarkable changing of the magnetic and electrical properties of the reoxidized compounds is a consequence of the L/Ba ordering and can be explained on the base of the Goodenough-Kanamori rules for 180° indirect superexchange interactions taking into account an ion size effect in A sublattice of perovskite.

DOI: 10.1103/PhysRevB.66.184424

PACS number(s): 75.30.Et, 74.25.Ha, 75.30.Vn, 75.50.Lk

#### I. INTRODUCTION

Manganites of  $L_{1-x}D_x$ MnO<sub>3</sub> type (L= rare-earth ion, D= alkaline-earth ion) exhibit a large variety of magnetic and crystal structure phase transformations with a sharp change of electrical transport properties. Hence they are appropriate objects to study the display between magnetic and electric states. Interesting features of manganites are phase transformations caused by orbital and charge states determining a type of magnetic ordering. For example, chargeordered compounds are antiferromagnetic insulators whereas charge disordered compounds are ferromagnetic metals.<sup>1,2</sup> An external magnetic field induces a transition from antiferromagnetic state to ferromagnetic one with the resistivity change by some orders of value.<sup>3,4</sup>

It is worth noting that to present there are manganites the most studied in which Ln ions are substituted with alkalineearth ions such as Ca and Sr.<sup>5–7</sup> This is partly associated with a wide concentration interval of *L* substitution for Ca and Sr, which is due to ion radii size of these elements. In the case of Ca at the synthesis in air there is a whole series of the solid solutions formed whereas in the case of Sr special conditions are necessary for this aim.<sup>8</sup> The solubility limit for the Ba ions is considerably lower. This is a consequence of the eventual formation of hexagonal BaMnO<sub>3</sub>-type perovskite at the grain boundaries. The small information volume about Ba-doped manganites is partly due to the impossibility to prepare high quality single crystals of designed composition by zone melting method.

By using Ba as a substituting ion the solid solutions are formed at the synthesis in air up to x=0.50.<sup>9</sup> Compositions  $La_{1-x}Ba_xMnO_3$  in the range  $0.20 \le x \le 0.50$  are metallic ferromagnets with a Curie point up to ~350 K.<sup>10</sup> In the case of rare-earth ions L=Pr, Nd the magnetic ordering temperature sharply decreases down to ~160 K  $(L=Pr)^{11-13}$  and ~80 K (L=Nd).<sup>14,15</sup> For Sm<sub>1-x</sub>Ba<sub>x</sub>MnO<sub>3</sub> series a substitution for Ba leads to a concentrational phase transition from an antiferromagnetic state (x < 0.12) into spin glass one ( $x \ge 0.12$ ) without ferromagnetic phase.<sup>15</sup> It is interesting to note that despite the large difference in L and Ba ionic radii the compositions with high Ba concentration have a cubic unit cell whereas solid solutions with rare earth substituted for Ca have an orthorhombically distorted unit cell.<sup>16</sup>

As it was reported<sup>12</sup> the  $Pr_{0.50}Ba_{0.50}MnO_{3-\gamma}$  composition prepared in strongly reducing conditions has a Curie temperature much larger in comparison with the composition obtained in air. Such a magnetic properties behavior is very unusual for manganites because for the case of  $La_{1-x}Ca_xMnO_{3-\gamma}$  (Ref. 17) and  $La_{1-x}Ba_xMnO_{3-\gamma}$  (Ref. 18) series is found the reduction to destroy the long-range magnetic order. Furthermore, strongly reduced compositions  $LaBaMn_2O_{5.5}$  and  $YBaMn_2O_5$  are known to be antiferromagnetic or ferrimagnetic insulators with relatively a large Néel point.<sup>19,20</sup> These compounds exhibit crystal ordering of La (Y) and Ba cations as well as oxygen vacancies. So we have studied in detail the properties of  $L_{0.50}Ba_{0.50}MnO_{3-\gamma}$ (L=Pr, Nd, Sm, Eu, Gd, Tb) compositions depending on the conditions of preparation. We have found these composition properties to be very sensitive to the crystallographic ordering of three-valent L and two-valent Ba ions in the A sublattice of the ABO<sub>3</sub> perovskite structure.

## **II. EXPERIMENTAL PROCEDURE**

Ceramic  $L_{0.50}$ Ba<sub>0.50</sub>MnO<sub>3</sub> (L=Pr,Nd,Sm,Eu,Gd,Tb) samples have been prepared using conventional ceramic technology. Oxides  $L_2O_3$ ,  $Mn_2O_3$  and carbonate BaCO<sub>3</sub> of high purity have been weighted in designed cation relation (L : Ba : Mn = 1 : 1 : 2) and ground thoroughly in an agate mortar by adding some quantity of ethyl alcohol. Before weighting  $L_2O_3$  has been annealed in air at 1000°C for 2 h to remove moisture and carbonic acid. The prepared oxides and carbonate mixtures have been pressed as pellets and then annealed in air at 1100°C during 2 h with following grind. The synthesis has been carried out in air at 1550°C during 2 h. In order to obtain compositions with an oxygen content close to stoichiometric one the samples have been placed on platinum substrate, annealed at 900°C in air during 100 h and then cooled to room temperature at a rate of  $100^{\circ}$ C h<sup>-1</sup>. The oxygen content value has been determined by termogravimetric analysis. According to our data the samples synthesized in air are stoichiometric in relation to the oxygen content. As it is well known the oxygen content in the obtained in air manganites strongly substituted by Ca and Sr ions is reported as close to stoichiometric.<sup>21</sup>

Reduced  $LBaMn_2O_5$  (L=Pr, Nd, Sm, Eu, Gd, Tb) samples were prepared by a topotactic reaction method. The doubling of the chemical formula is explained below. The samples were placed in evacuated silica ampoules with some quantity of metallic tantalum used as an oxygen getter. Silica ampoules were exposed at 900°C for 24 h and then cooled down to room temperature at a rate of  $100^{\circ}Ch^{-1}$ . The equation for the reduction chemical reaction is the following:

$$LBaMn_2O_6 + 0.4 \cdot Ta \rightarrow LBaMn_2O_5 + 0.2 \cdot Ta_2O_5.$$
 (1)

For the reduced samples the oxygen content has been determined from a mass loss by the sample weighting before and after reduction. To lower a relative error of oxygen content measurements the weight of the sample placed in silica ampoule was as a rule approximately 2-3 g. At such a condition the error value does not exceed 0.3%. The reduced samples have been then reoxidized in air at 900°C for 5 h. This reaction can be described by an equation:

PHYSICAL REVIEW B 66, 184424 (2002)

Thus three basic families of the samples have been obtained. Let us call and refer to these families as follows: (a) as-prepared disordered oxygen-stoichiometric  $L_{0.50}Ba_{0.50}MnO_3$ , (b) ordered oxygen-deficient LnBaMn<sub>2</sub>O<sub>5</sub>, and (c) reoxidized ordered oxygen-stoichiometric  $LBaMn_2O_6$ . The meaning of these abbreviations will be explained below.

Some samples with  $\gamma$  value intermediate between 0 and 1 have been received by the reoxidation in air at the selected thermal conditions. The variation of the physical properties of the *c* samples depending on the annealing temperature in air has been investigated. The *c* samples are annealed in air during 5 h step by step via 50°C up to 1350°C. Nominal chemical formula for the samples in view is  $LBaMn_2O_{6-\gamma\pm0.01}$ .

X-ray-diffraction (XRD) analysis of the reaction products has been performed using DRON-3 diffractometer in Cr- $K_{\alpha}$ radiation at room temperature in the angle interval 10°  $\leq 2 \Theta \leq 120^{\circ}$ . The electron diffraction (ED) study has been carried out with a JEM 200CX fitted with a tilting-rotating sample holder ( $\pm 60^{\circ}$ ). The high-resolution electron microscopy (HREM) studies have been performed using a TOP-CON 002B microscope with a point resolution of 1.7 Å. The PrBaMn<sub>2</sub>O<sub>6- $\gamma$ </sub> ( $\gamma$ =0.30) reoxidized sample for the electron microscopy has been prepared by crushing the crystallites in alcohol. The small flakes in suspension have been deposited on a holey carbon-coated film, supported by a copper grid.

The magnetization measurements have been performed using commercial vibrating sample magnetometer OI-3001 in the temperature interval 4–350 K. The magnetic transition temperature has been determined as that corresponding to the sharpest magnetization drop in a weak magnetic field. The resistivity measurements have been carried out using the samples with size of  $8 \times 2 \times 2$  mm<sup>3</sup> by usual four-probe method in the temperature interval 77–350 K. Magnetoresistance has been accounted as

$$MR(\%) = \{ [\rho(H) - \rho(0)] / \rho(0) \} \times 100\%, \qquad (3)$$

with  $\rho(H)$  resistivity in magnetic field of 9 kOe,  $\rho(0)$  resistivity in zero magnetic field. Magnetic field has been applied along electrical current in the sample.

### **III. EXPERIMENTAL RESULTS**

### A. Structural data

X-ray-diffraction patterns of  $LBaMn_2O_{6-\gamma}$  (L=Pr, Eu, Tb;  $\gamma=0$ , 1) compounds are presented in Fig. 1. These patterns are similar to those obtained for the samples on the base of other rare-earth ions. The analysis of the XRD patterns mainly indicates a single phase perovskite structure for all the samples. Existence of other phases is insignificant. However, the symmetry of unit cell is various for different samples. In the Table I there are unit-cell parameters presented for  $LBaMn_2O_{6-\gamma}$  (L=Pr,Nd,Sm,Eu,Gd,Tb) samples prepared in air (a), reduced in silica ampoules (b), and again reoxidized in air (c). The (a) samples prepared in air are

$$LBaMn_2O_5 + 0.5 \cdot O_2 \rightarrow LBaMn_2O_6.$$
 (2)



FIG. 1. Powder x-ray-diffraction patterns at room temperature for the  $LBaMn_2O_{6-\gamma}$  (L=Pr, Eu, Tb) samples: starting, prepared in air  $\gamma = 0$  (*a*); ordered, oxygen-deficient  $\gamma = 1$  (b); ordered, oxygen-stoichiometry  $\gamma = 0$  (c).

characterized with cubic unit cell whereas those in (b) reduced in silica ampoules are distorted tetragonally (Fig. 1). The cubic symmetry is in agreement with the complete disordering of  $L^{3+}$  and Ba<sup>2+</sup> ions on the A site of the perov-

skite cell. Parameter *c* for the tetragonally distorted (b) samples increases by 2 due to the ordering of  $L^{3+}$  and  $Ba^{2+}$  ions. The direct evidence of *A*-site ordering for (b) samples from XRD data is the (001) reflection which is well shown in

TABLE I. Unit-cell symmetry and parameters of  $LBaMn_2O_{6-\gamma}$  (L=Pr, Nd, Sm, Eu, Gd, Tb) samples, prepared in air ( $\gamma=0$ ) (a), reduced in the silica ampoules ( $\gamma=1$ ) (b), and annealed in air after reduction procedure ( $\gamma=0$ ) (c).

Composition	Synth. conditions	Symmetry	Ordering	a (Å)	b (Å)	c (Å)	V (Å <sup>3</sup> )
$\overline{\text{Pr}_{0.50}\text{Ba}_{0.50}\text{MnO}_3}$	a	cubic	disordered	3.901			59.37
PrBaMn <sub>2</sub> O <sub>5</sub>	b	tetragonal	ordered	3.975		7.798	123.10
PrBaMn <sub>2</sub> O <sub>6</sub>	с	tetragonal	ordered	3.900		7.775	118.26
Nd <sub>0.50</sub> Ba <sub>0.50</sub> MnO <sub>3</sub>	а	cubic	disordered	3.896			59.16
NdBaMn <sub>2</sub> O <sub>5</sub>	b	tetragonal	ordered	3.966		7.761	122.10
NdBaMn <sub>2</sub> O <sub>6</sub>	с	tetragonal	ordered	3.899		7.756	117.94
$Sm_{0.50}Ba_{0.50}MnO_3$	а	cubic	disordered	3.887			58.75
SmBaMn <sub>2</sub> O <sub>5</sub>	b	tetragonal	ordered	3.951		7.727	120.62
SmBaMn <sub>2</sub> O <sub>6</sub>	с	tetragonal	ordered	3.900		7.712	117.30
Eu <sub>0.50</sub> Ba <sub>0.50</sub> MnO <sub>3</sub>	а	cubic	disordered	3.881			58.47
EuBaMn <sub>2</sub> O <sub>5</sub>	b	tetragonal	ordered	3.945		7.712	120.03
EuBaMn <sub>2</sub> O <sub>6</sub>	с	orthorhombic	ordered	3.917	3.835	7.764	116.62
Gd <sub>0.50</sub> Ba <sub>0.50</sub> MnO <sub>3</sub>	а	cubic	disordered	3.879			58.39
GdBaMn <sub>2</sub> O <sub>5</sub>	b	tetragonal	ordered	3.942		7.704	119.73
GdBaMn <sub>2</sub> O <sub>6</sub>	с	tetragonal	ordered	3.901		7.651	116.47
Tb <sub>0.50</sub> Ba <sub>0.50</sub> MnO <sub>3</sub>	а	cubic	disordered	3.875			58.19
TbBaMn <sub>2</sub> O <sub>5</sub>	b	tetragonal	ordered	3.929		7.701	118.89
TbBaMn <sub>2</sub> O <sub>6</sub>	с	tetragonal	ordered	3.899		7.645	116.22



FIG. 2. Dependence of comparative volume of unit cell on rareearth ion radii for the  $LBaMn_2O_{6-\gamma}$  (L=Pr, Nd, Sm, Eu, Gd, Tb) samples: starting, prepared in air  $\gamma=0$  (a); ordered, oxygendeficient  $\gamma=1$  (b); ordered, oxygen-stoichiometry  $\gamma=1$  (c).

Figs. 1(b) and 1(c). It is placed around  $2\theta \sim 17^{\circ}$  and assures *A*-site modulation along the *c* axis. It is worth noting that the intensity of the (001) reflection is relatively weak because of the small contrast between  $L^{3+}$  and  $Ba^{2+}$  but it continuously rises with the number of rare-earth ions. It is probably because the (b) samples do not demonstrate complete ordering on the *A* site. However, it is clear only that the degree of the *A*-site ordering for the (b) samples is larger than that for the (a) samples. These considerable changes of crystal lattice allow us to examine the reduced (b) samples as individual compounds with doubled chemical formula  $LBaMn_2O_5$ .

The comparative unit-cell volume for all the samples decreases gradually as rare-earth ion number increases due to ionic radii lowering (Fig. 2). The (b) samples corresponding to a definite type of rare-earth ion are characterized with much larger unit-cell volume. This is probably caused by increasing manganese ion size as a result of its oxidative state decrease.<sup>22</sup> The nominal chemical formula of the (b) samples is  $LBa(Mn^{2+}Mn^{3+})O_5$ .

A typical [100] ED pattern for intermediate  $PrBaMn_2O_{6-\gamma}$  ( $\gamma=0.30$ ) reoxidized sample is given in Fig. 3(a). A reconstruction of the reciprocal space, carried out with a JEOL 200CX electron microscope, evidenced a tetragonal cell with  $a = a_p \approx 3.9$  Å and  $c \approx 2a_p$  ( $a_p$  is the parameter of the ideal perovskite unit cell); there is no condition limiting the reflection. These cell parameters are similar to those for the structure of a double perovskite, as observed for LaBaMn\_2O\_{6-\gamma},<sup>11</sup> with oxygen-deficient [PrO<sub>z</sub>] and oxygenated [BaO] layers alternating along *c*. The extra reflections involving the doubling of the *c* parameter are more or less intense depending on the crystallites (for similar crystal thicknesses).

The simulated [100] ED patterns were calculated using MacTempas software and the atomic positions of the ordered LaBaMn<sub>2</sub>O<sub>6- $\gamma$ </sub> perovskite.<sup>23</sup> Two examples of simulated [100] ED patterns for  $\gamma$ =0 and  $\gamma$ =1 samples are given in Fig. 4, calculated for a crystal thickness close to 10 nm and



FIG. 3. Experimental [100] ED pattern for the intermediate PrBaMn<sub>2</sub>O<sub>6- $\gamma$ </sub> ( $\gamma$ =0.30) sample (a). The intense reflections are those of the perovskite subcell and the weaker ones evidence a superstructure with  $c=2a_p$ . Two perpendicular systems are superimposed, due to a twinning phenomenon. Corresponding [100] HREM image for the intermediate PrBaMn<sub>2</sub>O<sub>6- $\gamma$ </sub> ( $\gamma$ =0.30) sample (b), recorded for a focus value close to -30 nm.

the two limit oxygen contents, namely  $O_5$  and  $O_6$ . They show that the intensity of the extra reflections is sensitive to the oxygen content. In the example given in Fig. 3(a), the extra reflections are rather intense; two reflections, 001 and  $001_{\perp}$  belonging to two perpendicular  $c^*$  axes, are indicated by arrows. They are the signatures of twinning domains, observed in numerous crystallites because the superstructure  $(2a_p)$  could be established along the three equivalent  $\{100\}_p$ directions of the perovskite unit cell.

The doubling of the periodicity along c is clearly visible in the [100] HREM images, for several defocus values. One example is given in Fig. 3(b), for a focus value close to -30 nm, i.e., the Scherzer value, which is sensitive to the



FIG. 4. Calculated [100] ED patterns for an ordered, oxygenstoichiometry  $PrBaMn_2O_6$  double perovskite ( $O_6$ ) and ordered, oxygen-deficient  $PrBaMn_2O_5$  one ( $O_5$ ).



FIG. 5. Magnetization vs temperature in a field of 100 Oe after field cooling (FC) and zero-field cooling (ZFC) for the  $LBaMn_2O_{6-\gamma}$  (L=Pr,Eu,Tb) samples: starting, prepared in air ( $\gamma=0$ ) (a); ordered, oxygen-deficient ( $\gamma=1$ ) (b); ordered, oxygen-stoichiometry ( $\gamma=0$ ) (c).

oxygen atoms displacement and to oxygen deficiency; in this image, the bright dots are correlated to the light electron density zones. The main characteristic of the contrast consists of two types of parallel rows of bright dots, spaced by 3.9 Å along *b*. The brighter dots are correlated to the positions of the oxygen atoms and oxygen vacancies in the oxygen-deficient [PrO<sub>z</sub>] layers, and the less bright ones to the oxygen positions of the oxygenated [BaO] layers. Lastly, the small gray dots located in between these rows are correlated to the oxygen positions of the [MnO<sub>2</sub>] layers. The XRD and ED patterns as well as HREM images show that the ions and oxygen vacancies ordering mechanism is well established for the LBaMn<sub>2</sub>O<sub>6-γ</sub> (b) and (c) samples.

After the reoxidation procedure almost all from the  $LBaMn_2O_6$  (c) samples retain the tetragonal symmetry of the unit cell. In our opinion, this fact confirms the ordered distribution of  $L^{3+}$  and  $Ba^{2+}$  ions. The (001) reflection for the (c) samples is also clear shown in Fig. 1(c) similar to the (b) samples. The *A*-site ordering for the YBaMn\_2O\_6 compound from XRD measurements has been earlier established<sup>24</sup> too. Only the reoxidized oxygen-stoichiometry EuBaMn\_2O\_6 (c) sample (one from others) has the orthorhombic unit cell (Fig. 1). The crystal lattice distortions gradually increase with increasing rare-earth ion number likely due to the rise of the rare-earth and barium ion radii mismatch.

It is worth noting that the comparative volumes per formula unit are approximately equal to the samples obtained in air (a) and those reoxidized after reduction (c) although in the second case they are slightly less (Fig. 2). Tetragonal distortions mainly for the PrBaMn<sub>2</sub>O<sub>6</sub> and NdBaMn<sub>2</sub>O<sub>6</sub> (c) samples are sufficiently decreased after annealing in air at 1100°C and removed completely after annealing at 1300°C.

It should be noted that the half width at half maximum of the x-ray peaks for the (b) and (c) samples is enough large ( $\approx 1^{\circ}$ ). This fact probably indicates that the samples in view are spatial nonhomogeneous. The widening of the x-ray peaks may be result of both the defects and microstrains over the crystal lattice. This is a consequence of the reduction procedure. It is likely that the complete deoxygenation is not reached for (c) samples and few grains have various oxygen content slightly differed from stoichiometric.

#### **B.** Magnetic properties

Results of the magnetization measurements for  $LBaMn_2O_{6-\gamma}$  (L=Pr, Eu, Tb;  $\gamma=0$ , 1) samples performed in a relatively weak magnetic field of 100 Oe in dependence on temperature for all the samples after cooling in field (FC) and in zero field (ZFC) are presented in Fig. 5.

 $Pr_{0.50}Ba_{0.50}MnO_3$  (a) sample is characterized by magnetic ordering temperature  $T_{MO} \sim 140$  K and spontaneous magnetic moment  $M_S \sim 2.6\mu_B/f.u.$  (Fig. 6) that is less value in comparison with the calculated one in the case of parallel orientation of manganese moments  $[\mu(Mn^{3+})\approx 4\mu_B]$  and  $\mu(Mn^{4+})\approx 3\mu_B]$ . It is possible that some domains of the sample are antiferromagnetic because the boundary of the concentrational ferromagnetic-antiferromagnetic transition in the  $L_{1-x}Ba_xMnO_3$  series is very close to x=0.5.<sup>10,11</sup> ZFC and FC magnetization curves are very close. This indicates a small magnetic anisotropy.



FIG. 6. Magnetization vs field at T=15 K for the  $LBaMn_2O_{6-\gamma}$  (L=Pr,Eu,Tb) samples: starting, prepared in air ( $\gamma=0$ ) (*a*); ordered, oxygen-deficient ( $\gamma=1$ ) (b); ordered, oxygen-stoichiometry ( $\gamma=0$ ) (c).

PrBa(Mn<sup>3+</sup>Mn<sup>2+</sup>)O<sub>5</sub> (b) sample exhibits  $T_{MO} \approx 125$  K. The ZFC curve shows a weak peak around  $T_{MO}$ . Such a type of ZFC and FC behavior may be attributed to strongly anisotropic ferro- or ferrimagnets. However, the spontaneous magnetic moment is very small (about  $0.11\mu_B$  per Mn ion). After the reoxidation procedure both  $T_{MO}$  and M<sub>S</sub> are too much large for the PrBaMn<sub>2</sub>O<sub>6</sub> (c) sample. It is notable the  $T_{MO}$  is equal to 320 K that is two times as large as for the starting Pr<sub>0.50</sub>Ba<sub>0.50</sub>MnO<sub>3</sub> *a* compound. Ordering of Nd and Ba cations after the reoxidation procedure leads to enhancement of  $T_{MO}$  from 80 to 310 K.

The Eu<sub>0.50</sub>Ba<sub>0.50</sub>MnO<sub>3</sub> (a) sample before reduction is probably spin glass (Fig. 5) with temperature of magnetic moments freezing  $T_f \approx 40$  K. The EuBa(Mn<sup>3+</sup>Mn<sup>2+</sup>)O<sub>5</sub> (b) sample is characterized with low spontaneous moment value ~0.1 $\mu_B$ /Mn (Fig. 6), however, the temperature of transition into the paramagnetic state increases up to 150 K. ZFC and FC magnetization curves differ significantly, which is possible in the case of large magnetic anisotropy. The transition to the paramagnetic state is rather sharp, which is characteristic of homogeneous in magnetic aspect magnetic materials. The EuBa(Mn<sup>2+</sup>Mn<sup>3+</sup>)O<sub>5</sub> (b) sample demonstrates astonishing magnetic properties at low-temperature regime. The FC curve slightly decreases about 40–50 K.

After the annealing in air of the EuBa(Mn<sup>2+</sup>Mn<sup>3+</sup>)O<sub>5</sub> (b) sample the dramatic increase of the spontaneous magnetization and Curie point up to  $\sim 0.5 \mu_B/Mn$  and  $\sim 260$  K, respectively, has been revealed too (Fig. 6). However, the spontaneous magnetization is still much less than one could expect in the case of pure ferromagnetic ordering.

The Tb<sub>0.50</sub>Ba<sub>0.50</sub>MnO<sub>3</sub> (a) sample prepared in air shows also the static magnetic properties typical for the spin-glass state. The ZFC magnetization curve has a maximum about 40 K (Fig. 5). Near this temperature ZFC and FC curves are diverged, and the spontaneous magnetization occurs. Magnetization is not saturated in the field up to 16 kOe (Fig. 6). The sharp FC magnetization increase by lowering temperature is caused the most probably by Tb-sublattice contribution because the magnetic moment of Tb<sup>3+</sup> is very large,  $\sim 10\mu_B$ .<sup>25</sup> The M(H) curve has a Langevin form peculiar to cluster magnetic systems.

The long-range magnetic order occurs in the reduced TbBa( $Mn^{3+}Mn^{2+}$ )O<sub>5</sub> (b) sample at temperature near 165 K (Fig. 5). The anomalous behavior around  $T_N$  is not pronounced apparently due to the Tb-sublattice contribution directed opposite to the Mn one by almost compensating it. Contrary to EuBa( $Mn^{3+}Mn^{2+}$ )O<sub>5</sub> the spontaneous magnetization is rather large. Spontaneous magnetic moment per Mn ion is difficult to account for because of sufficient paramagnetic contribution of Tb<sup>3+</sup> ions. At temperature near 100 K the compensation point has been observed conditioned the most probably by the fact the Tb-sublattice contribution opposite to the Mn ions moment increases gradually as in the case of rare-earth ferrimagnetic garnets.<sup>26</sup>

Though there is a divergence observed in ZFC and FC magnetizations behavior for the annealed in air TbBaMn<sub>2</sub>O<sub>6</sub> (c) sample at temperature near 160 K, the smoothness of magnetization curves seems to be incompatible with cooperative magnetic ordering. However, the large magnetic contribution from the Tb sublattice may mask the magnetic phase transition. One could suppose the magnetic properties of the TbBaMn<sub>2</sub>O<sub>6</sub> (c) sample annealed in air after reduction in silica ampoule to be caused with ferromagnetic clusters with strong magnetic interactions between manganese ions. The ferromagnetic clusters are enclosed in paramagnetic or antiferromagnetic matrix. Such a model does not contradict to the observed data. The results of the magnetic properties studied for all the compounds are shown in Table II.

#### C. Electrical properties

Resistivity and magnetoresistance vs temperature for the starting  $L_{0.50}Ba_{0.50}MnO_3$  (a) and ordered  $LBaMn_2O_6$  (L = Pr, Nd, Sm, Eu, Gd, Tb) (c) samples annealed in air after reduction are displayed in Fig. 7.

For  $L_{0.50}$ Ba<sub>0.50</sub>MnO<sub>3</sub> (L=Pr, Nd) (a) samples prepared in air there is a classic resistivity and magnetoresistance behavior revealed inherent in magnetic semiconductors with metalinsulator transition near the  $T_C$  and magnetoresistance peak of ~47 and 65%, respectively. However,  $L_{0.50}$ Ba<sub>0.50</sub>MnO<sub>3</sub> (L=Sm, Eu, Gd, Tb) (a) compounds do not exhibit metalinsulator transition and magnetoresistance peak, which agrees with magnetic data (Fig. 5).

All the reduced  $LBaMn_2O_5$  (b) samples have an activated type of conductivity and are characterized with high resistivity even near room temperature. It is worth to note that the (c) samples annealed in air at temperatures above 1300°C have the magnetic and electrical properties similar to those for the (a) samples prepared in air.

TABLE II. Magnetic state, critical temperature, and evaluated spontaneous magnetic moment per Mn ion for  $LBaMn_2O_{6-\gamma}$  (L=Pr, Nd, Sm, Eu, Gd, Tb) samples, prepared in air ( $\gamma=0$ ) (a), reduced in the silica ampoules ( $\gamma=1$ ) (b) and annealed in air after reduction procedure ( $\gamma=0$ ) (c). F denotes ferromagnetic state; FI: ferrimagnetic one; SG: state with spin-glass properties; F+A: ferromagnet with antiferromagnetic clusters;  $F_{cl}+P$ : mixture of ferromagnetic clusters and paramagnetic phase; F+P: inhomogeneous ferromagnet.

Composition	Synth. conditions	Ordering	Magnetic state	$T_{MO}$ (K)	$M_S (\mu_B/{ m Mn})$
Pr <sub>0.50</sub> Ba <sub>0.50</sub> MnO <sub>3</sub>	а	disordered	F+A	140	2.61
PrBaMn <sub>2</sub> O <sub>5</sub>	b	ordered	FI	125	0.11
PrBaMn <sub>2</sub> O <sub>6</sub>	с	ordered	F	320	2.58
Nd <sub>0.50</sub> Ba <sub>0.50</sub> MnO <sub>3</sub>	а	disordered	F+A	80	3.06
NdBaMn <sub>2</sub> O <sub>5</sub>	b	ordered	FI	130	0.23
NdBaMn <sub>2</sub> O <sub>6</sub>	с	ordered	F	310	2.94
$Sm_{0.50}Ba_{0.50}MnO_3$	а	disordered	SG	45	
$SmBaMn_2O_5$	b	ordered	FI	140	0.19
$SmBaMn_2O_6$	с	ordered	F+P	280	1.24
Eu <sub>0.50</sub> Ba <sub>0.50</sub> MnO <sub>3</sub>	а	disordered	SG	40	
EuBaMn <sub>2</sub> O <sub>5</sub>	b	ordered	FI	150	0.10
EuBaMn <sub>2</sub> O <sub>6</sub>	с	ordered	F+P	260	0.52
Gd <sub>0.50</sub> Ba <sub>0.50</sub> MnO <sub>3</sub>	а	disordered	SG	40	
$GdBaMn_2O_5$	b	ordered	FI	155	0.92
$GdBaMn_2O_6$	с	ordered	F+P	250	0.28
$\mathrm{Tb}_{0.50}\mathrm{Ba}_{0.50}\mathrm{MnO}_3$	а	disordered	SG	40	
$TbBaMn_2O_5$	b	ordered	FI	165	1.33
TbBaMn <sub>2</sub> O <sub>6</sub>	с	ordered	$\mathbf{F}_{cl} + \mathbf{P}$	160	

For  $LBaMn_2O_6$  (L=Pr, Nd, Sm) (c) samples reoxidized in air at temperature of 900°C the resistivity in the magnetically ordered state starts to decrease as temperature decreases, however the temperature corresponding to the maximal resistivity value does not coincide with the Curie point. Near the Curie point there is a maximum of magnetoresistance observed as in the case of classic magnetic semiconductors. The gradual magnetoresistance increase has been observed as temperature decreased that is characteristic of conducting magnetic ceramics. This type of magnetoresistance is due to an intergranular electrical transport. The ordered  $LBaMn_2O_6$  (L=Gd, Tb) (c) samples annealed in air



FIG. 7. Resistivity and magnetoresistance in a field of 9 kOe vs temperature for the  $L_{0.50}Ba_{0.50}MnO_3$  starting, prepared in air samples (a) and  $LBaMn_2O_6$  (L=Pr, Nd, Sm, Eu, Gd, Tb) ordered, oxygenstoichiometry samples (c).

after reduction exhibit a gradual increase of both resistivity and magnetoresistance as temperature decreases down to 77 K (Fig. 7).

## **IV. DISCUSSION**

First, let us consider an origin of the magnetic state of the (a) samples obtained in air. The magnetic state of  $L_{1-x}D_x$ MnO<sub>3</sub> (D=Ca, Sr, Ba, Pb) manganites is known to be determined with Mn<sup>3+</sup>/Mn<sup>4+</sup> relation in the *B* sublattice of the  $ABO_3$  perovskite,<sup>5</sup> average radii of alkaline-earth and rare-earth ions  $\langle r_A \rangle$ ,<sup>27,28</sup> as well as the value of cation size mismatch in *A* sublattice:

$$\sigma^2 = \sum x_i r_i^2 - \langle r_A \rangle^2, \tag{4}$$

where  $x_i$  is a part of the perovskite *A* sublattice filled by the *i*th-type cation (fractional occupancy) with corresponding radius  $r_i$ ,  $\langle r_A \rangle$ -an average ionic radius of the *A* sublattice. This discrepancy value (variance) characterizes a mismatch between alkaline-earth and rare-earth ionic radii.<sup>29</sup>

At the  $Mn^{3+}/Mn^{4+}$  relation close to 1:1 the ferromagnetic state transforms into antiferromagnetic one as  $Mn^{4+}$  ions concentration increases.<sup>30</sup> The less an average ionic radius of A-sublattice and the more the Ln and D ionic radii mismatch the lower magnetic ordering temperature is as a rule.<sup>27</sup>

Magnetic properties of the  $L_{0.50}Ba_{0.50}MnO_3$  (a) system agree with such a scheme. The compounds based on relatively large rare-earth ions such as La, Pr, Nd are ferromagnetic metals with  $T_C = 270$ ,<sup>10</sup> 140, 80 K, respectively, whereas the compounds on the base of the smaller ions such as Sm, Eu, Gd, Tb exhibit properties similar to spin glass with temperature of magnetic moments freezing  $T_f \sim 40$  K and semiconductive character of conductivity (Figs. 7 and 8). The magnetic moment value revealed in  $L_{0.50}Ba_{0.50}MnO_3$ (L=Pr, Nd) corresponds apparently to the two phase state: the main phase is ferromagnetic and insignificant inclusions of antiferromagnetic phase are present. Just in such a way in the case of  $L_{1-x}Ca_xMnO_3$  and  $L_{1-x}Sr_xMnO_3$  perovskites one could explain the lowered magnetization values in comparison with expected ones for ferromagnetic ordering.<sup>31</sup>

The spin-glass state probably results from a large difference in the local distribution of the Mn-O-Mn bond angle values caused in its turn with a large mismatch of L and D ionic radii. Really, the larger an  $\langle r_A \rangle$  average ionic radius of A sublattice the less  $\langle Mn-O-Mn \rangle$  average bond angle value differs from 180°. According to the empirical Goodenough-Kanamori rules for 180° indirect superexchange interactions the closer the  $\langle Mn-O-Mn \rangle$  average bond angle to 180° the larger the exchange interaction value.<sup>32–34</sup> In the case of the orbitally disordered state the sign of exchange interaction can change from positive to negative as  $\langle Mn-O-Mn \rangle$  angle decreases. As L and D ions are distributed randomly in the A sublattice the local dispersion of the Mn-O-Mn angle values are presumably below some critical magnitude at which the ferromagnetic properties can appear. The magnetic state



FIG. 8. Dependence of magnetic state on the rare-earth ion radii for the  $LBaMn_2O_{6-\gamma}$  (L=La, Pr, Nd, Sm, Eu, Gd, Tb, Y) samples: starting, prepared in air ( $\gamma=0$ ) (a); ordered, oxygen-deficient ( $\gamma$ = 1) (b); ordered, oxygen-stoichiometry ( $\gamma=0$ ) (c). F denotes ferromagnetic state, F+A: mixture of ferromagnetic and antiferromagnetic phases; SG: spin glass; FI: ferrimagnetic;  $F_{cl}$ +P: mixture of ferromagnetic clusters and paramagnetic phase; F+P: inhomogeneous ferromagnet; P: paramagnet.

similar to spin-glass type occurs as a result of the competition between randomly distributed ferromagnetic and antiferromagnetic interactions.

By reducing  $L_{0.50}Ba_{0.50}MnO_3$  (a) compositions up to  $LBaMn_2O_5$  (b) ones there is an ordering of *L* and Ba cations in *A*-sublattice and oxygen vacancies occurred as it was revealed in the case of  $LBaMn_2O_5$  (L=La, Y).<sup>10,20</sup> It is clearly determined that there are (001) planes presented in these compounds alternating along *c* axis of the tetragonal unit cell and filled predominantly with either Ba or *L* ions. A similar crystal structure is also observed in the case of  $LBaCo_2O_5$  cobaltites.<sup>35</sup>

The sharp transition to the paramagnetic state for the  $LBaMn_2O_5$  (b) samples series evidences the well determined magnetic order. According to Ref. 20 the magnetic structure of YBaMn\_2O\_5 is determined with an opposite orientation of Mn<sup>3+</sup> and Mn<sup>2+</sup> magnetic ions. Unfortunately the sample used<sup>20</sup> for neutron-diffraction study contains only ~30% of the YBaMn\_2O\_5 phase, which strongly reduces the reliability of the results. In the case of opposite orientation of Mn<sup>3+</sup> and Mn<sup>2+</sup> magnetic moments a total magnetic moment per formula unit should be close to  $1\mu_B/f.u.$ , however, magnetic measurements have given a lower value ~ $0.5\mu_B/f.u.$  In principle a weak ferromagnetic moment can result from Dzialoshinsky-Moriya asymmetric exchange, however, it is

unlikely for considered compounds for symmetry aspects and a rather large magnetization.

According to Goodenough-Kanamori rules the 180° magnetic superexchange interactions between  $Mn^{2+}$  and  $Mn^{3+}$  cations are predominantly antiferromagnetic if  $Mn^{2+}$  and  $Mn^{3+}$  are randomly distributed over the lattice. Since the magnetic moments of the  $Mn^{2+}$  and  $Mn^{3+}$  cations are different the true magnetic state for the  $LBaMn_2O_5$  (b) compounds is ferrimagnetic with total magnetic moment of  $1 \mu_B/f.u.$ 

We believe the most likely magnetic structure of the  $LBaMn_2O_5$  (b) compounds is determined by partial ordering of  $Mn^{2+}$  and  $Mn^{3+}$  cations in a chesslike manner (*G* type of magnetic structure). In this type of ordering every  $Mn^{2+}$  cation is surrounded by six  $Mn^{3+}$  ones and vice versa. For  $LBaMn_2O_5$  (b) samples every  $Mn^{2+}$  is connected directly via oxygen anions with five  $Mn^{3+}$ . In the case of noncomplete longe-range ordering of  $Mn^{2+}$  and  $Mn^{3+}$  cations the total magnetic moment should be smaller than  $1\mu_B/f.u$ .

The long-range crystallographic order in L and Ba ions distribution remains after annealing in air unless the temperature of annealing is above 1300°C. This is evidenced with superstructure reflexitons and tetragonal distortions from x-ray as well as doubling effects from ED and HREM investigations for the (c) samples annealed in air after reduction in silica ampoules. The ordering of cations in A sublattice probably leads to translation symmetry in an arrangement of Mn-O-Mn bond angles in the *B* sublattice as well as to decrease the Mn-O bond lengths and as a consequence to the appearance of conditions at which ferromagnetism can occur. Note that the Mn-O-Mn bond angles ordering and their enhancing can also lead to a sharp increase of the magnetic ordering temperature. It is possible that the A-site ordering suppresses the mismatch effect.

It is reasonable to propose that the compounds with large ionic radius of L are ferromagnets whereas as L radius decreases they are nonhomogeneous ferromagnets which is shown with the strong drop in spontaneous magnetization. Such a type of magnetic behavior could be also attributed to noncollinear or ferrimagnetic ordering. However, the transition from paramagnetic to magnetically ordered state is not pronounced contrary to the  $LBaMn_2O_5$  series. For example, ZFC and FC magnetizations for TbBaMn\_2O\_6 series gradually diverge without anomaly behavior indicating magnetic phase transition. It should be noted that the magnetic nonhomogeneous state may be also a result of the spatial hetero-

\*Corresponding author: Electronic address: truhanov@ifttp.basnet.by

- <sup>1</sup>Y. Tokura and Y. Tomioka, J. Magn. Magn. Mater. **200**, 1 (1999).
- <sup>2</sup>J.M.D. Coey, M. Viret, and S. von Molnár, Adv. Phys. **48**, 167 (1999).
- <sup>3</sup>Y. Tomioka, A. Asamitsu, Y. Moritomo, H. Kuwahara, and Y. Tokura, Phys. Rev. Lett. **74**, 5108 (1995).
- <sup>4</sup>M. Tokunaga, N. Miura, Y. Tomioka, and Y. Tokura, Phys. Rev. B 57, 5259 (1998).
- <sup>5</sup>G.H. Jonker and J.H. Van Santen, Physica (Utrecht) 16, 337

geneity observed by the XRD measurements.  $LBaMn_2O_5$  (a) samples also exhibit broad x-ray peaks whereas the transition to the paramagnetic state is sharp. Hence we suppose that a magnetically nonuniform state is more likely in comparison with the homogeneous canted antiferromagnet one. In order to elucidate in detail the crystal and magnetic structure of these compounds it is necessary to perform neutron-diffraction studies.

### V. CONCLUSION

In summary, we have obtained three families of the manganites half doped by Ba ions using reduction-oxidation synthesis : (a) as-prepared disordered oxygen-stoichiometric  $L_{0.50}$ Ba<sub>0.50</sub>MnO<sub>3</sub>, (b) ordered oxygen-deficient LBaMn<sub>2</sub>O<sub>5</sub>, and (c) reoxidized ordered oxygen-stoichiometric  $LBaMn_2O_6$ . We have studied the crystal structure peculiarities as well as magnetic and electrical properties of these compounds. For the (a) compounds it is established that those based on relatively large rare-earth ions are ferromagnetic metals whereas the compounds on the base of the smaller ions exhibit properties similar to spin glass and a semiconductive character of conductivity. It is observed that the (b) compounds are characterized by  $L^{3+}$  and  $Ba^{2+}$  ordering in (001) planes, oxygen vacancies ordering, and its location in  $L^{3+}$  layers. It is more likely that the (b) samples are ferrimagnets with  $T_N$  continuously increased as the number of rare-earth ion rises. For the (c) samples A-site ordering retains and as consequence the  $T_C$  strongly increases. It is established that the cation ordering effects play an important role in directing the physical properties of the manganites. It is supposed that the remarkable changing of the magnetic and electrical properties of the (c) compounds is a consequence of the L/Ba ordering and can be explained on the base of the Goodenough-Kanamori rules for 180° indirect superexchange interactions taking into account an ion size effect in the A sublattice of perovskite.

## ACKNOWLEDGMENTS

This work was partly supported by Fund for Fundamental Research of the Republic of Belarus (project No. F02R-122) and the Polish Committee of Science (KBN Grant No. 5 P03B 016 20). The authors would like to thank D. G. Vas'kov and M. V. Bushinskiy for help during preparation of the paper.

- <sup>6</sup>G. Matsumoto, J. Phys. Soc. Jpn. **29**, 606 (1970).
- <sup>7</sup>A. Urushibara, Y. Moritomo, T. Arima, A. Asamitsu, G. Kido, and Y. Tokura, Phys. Rev. B **51**, 14103 (1995).
- <sup>8</sup>K. Kikuchi, H. Chiba, M. Kikuchi, and Y. Syono, J. Solid State Chem. **146**, 1 (1999).
- <sup>9</sup>B. Raveau, C. Martin, A. Maignan, and M. Hervieu, J. Phys.: Condens. Matter 14, 1297 (2002).
- <sup>10</sup>F. Millange, V. Caignaert, B. Domengés, B. Raveau, and E. Suard, Chem. Mater. **10**, 1974 (1998).
- <sup>11</sup>A. Barnabé, F. Millange, A. Maignan, M. Hervieu, B. Raveau, G.

<sup>&</sup>lt;sup>†</sup>Electronic address: troyan@ifttp.bas-net.by

<sup>(1950).</sup> 

Van Tendeloo, and P. Laffez, Chem. Mater. 10, 252 (1998).

- <sup>12</sup>I.O. Troyanchuk, S.V. Trukhanov, H. Szymczak, and K. Bärner, J. Phys.: Condens. Matter **12**, L155 (2000).
- <sup>13</sup>S.V. Trukhanov, I.O. Troyanchuk, I.M. Fita, H. Szymczak, and K. Bärner, J. Magn. Magn. Mater. **237**, 276 (2001).
- <sup>14</sup>S.V. Trukhanov, I.O. Troyanchuk, D.D. Khalyavin, I.M. Fita, H. Szymczak, and K. Bärner, Sov. Phys. JETP **94**, 329 (2002).
- <sup>15</sup>I.O. Troyanchuk, D.D. Khalyavin, S.V. Trukhanov, and H. Szymczak, J. Phys.: Condens. Matter **11**, 8707 (1999).
- <sup>16</sup>I.O. Troyanchuk, S.V. Trukhanov, H. Szymczak, J. Przewoznik, and K. Bärner, Sov. Phys. JETP **93**, 161 (2001).
- <sup>17</sup>J.M. González-Calbet, E. Herrero, N. Rangavittal, J.M. Alonso, J.L. Martínez, and M. Vallet-Regí, J. Solid State Chem. **148**, 158 (1999).
- <sup>18</sup>H.L. Ju, J. Gopalakrishnan, J.L. Peng, Qi Li, G.C. Xiong, T. Venkatesan, and R.L. Greene, Phys. Rev. B **51**, 6143 (1995).
- <sup>19</sup>V. Caignaert, F. Millange, B. Domengés, and B. Raveau, Chem. Mater. **11**, 930 (1999).
- <sup>20</sup>J.A. McAllister and J.P. Attfield, J. Mater. Chem. 8, 1291 (1998).
- <sup>21</sup>P. Schiffer, A.P. Ramirez, W. Bao, and S-W. Cheong, Phys. Rev. Lett. **75**, 3336 (1995).
- <sup>22</sup>R.D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **32**, 751 (1976).

- <sup>23</sup>F. Millange, A. Maignan, V. Caignaert, M. Hervieu, and B. Raveau, Z. Phys. B: Condens. Matter **101**, 169 (1996).
- <sup>24</sup>T. Nakajima, H. Kageyama, and Y. Ueda, J. Phys. Chem. Solids 63, 913 (2002).
- <sup>25</sup>R. Bidaux, J.E. Bouree, and J. Hammann, J. Phys. (Paris) **36**, 803 (1975).
- <sup>26</sup>J.D. Cashion, A.H. Cooke, D.M. Martin, and M.R. Wells, J. Appl. Phys. **41**, 1193 (1970).
- <sup>27</sup>L.M. Rodriguez-Martinez and J.P. Attfield, Phys. Rev. B 58, 2426 (1998).
- <sup>28</sup>R. Mahesh and M. Itoh, Phys. Rev. B 60, 2994 (1999).
- <sup>29</sup>P.V. Vanitha, P.N. Santosh, R.S. Sing, C.N.R. Rao, and J.P. Attfield, Phys. Rev. B **59**, 13539 (1999).
- <sup>30</sup>H. Fujishiro, M. Ikebe, and Y. Konno, J. Phys. Soc. Jpn. **67**, 1799 (1998).
- <sup>31</sup>S.V. Trukhanov, I.O. Troyanchuk, F.P. Korshunov, V.A. Sirenko, H. Szymczak, and K. Bärner, Low Temp. Phys. 27, 283 (2001).
- <sup>32</sup>J.B. Goodenough, Phys. Rev. **100**, 564 (1955).
- <sup>33</sup>J.B. Goodenough, A. Wold, R.J. Arnott, and N. Menyuk, Phys. Rev. **124**, 373 (1961).
- <sup>34</sup>E.E. Havinga, Philips Res. Rep. **21**, 432 (1966).
- <sup>35</sup>E. Suard, F. Fauth, V. Caignaert, I. Mirebeau, and G. Baldinozzi, Phys. Rev. B **61**, R11 871 (2000).