

# Short-range magnetic order in the paramagnetic phase of cubic SrMnO<sub>3-x</sub> ( $x < 0.005$ ): An <sup>17</sup>O and <sup>87</sup>Sr NMR study

A. Gerashenko,<sup>1,2</sup> A. Trokiner<sup>2</sup>, S. Verkhovskii<sup>1,2</sup>, Z. Volkova,<sup>1</sup> A. Germov<sup>1</sup>, K. Mikhalev,<sup>1</sup> and A. Yakubovskii<sup>3</sup>

<sup>1</sup>Mikheev Institute of Metal Physics, Ural Branch of Russian Academy of Sciences, 620108 Ekaterinburg, Russia

<sup>2</sup>LPEM UMR8213, ESPCI Paris, PSL Research University, CNRS, Sorbonne University, 10 rue Vauquelin, Paris, France

<sup>3</sup>Russian Research Centre “Kurchatov Institute,” 123182 Moscow, Russia



(Received 29 April 2020; revised 30 July 2020; accepted 15 September 2020; published 8 October 2020)

In the paramagnetic phase of cubic antiferromagnet SrMnO<sub>2.997</sub> ( $T_N = 236$  K), the spin susceptibility of the localized Mn( $t_{2g}$ ) electrons exhibits a gapped behavior with  $d\chi_s(T) \geq 0$ , suggesting the existence of a low-dimensional short-range magnetic order above  $T_N$ . The low-frequency fluctuations of the spin correlations of neighboring Mn<sup>4+</sup> ions were probed by measuring the spin-lattice relaxation rate  $T_1^{-1}$  and the echo-decay rate  $T_2^{-1}$  of <sup>17</sup>O and <sup>87</sup>Sr nuclei up to 420 K. <sup>17</sup>O being involved in an Mn–O–Mn bond, the echo-decay rate  $^{17}T_2^{-1}$  probes the fluctuations of the two neighboring  $S(t_{2g})$  spins at low frequency,  $\omega \leq 10^3$  s<sup>-1</sup>. It is shown that there exist local changes of the double-exchange interaction, which favor FM correlated pairs of neighboring  $S(t_{2g})$  spins in the Mn–<sup>17</sup>O–Mn bond. The unusual thermal behavior of  $^{17}T_2^{-1}(T)$  indicates low-frequency fluctuations of the short-range magnetic order which may include the change of AF  $\leftrightarrow$  FM spin alignment of neighboring magnetic ions. For <sup>87</sup>Sr nuclei, which probe the spin configuration of eight neighboring Mn ions in the cubic unit cell,  $^{87}T_2^{-1}$  has no such anomaly, implying that FM order should be excluded within the cubic unit cell. With both NMR probes, it is deduced that the only magnetic orders which may exist in the cubic unit cells are the following: AF–G [ $\mathbf{q} = \pi/a(1, 1, 1)$ ], AF–C [ $\mathbf{q} = \pi/a(1, 1, 0)$ ], and AF–A [ $\mathbf{q} = \pi/a(0, 0, 1)$ ] so that the slow fluctuating short-range magnetic order is built from these three AF ordered unit cells. Furthermore, we deduce from  $^{17}T_1^{-1}$  results that the fluctuating short-range magnetic order, i.e., corresponding to large  $q$ , has a high thermal stability in the PM phase of SrMnO<sub>2.997</sub>.

DOI: [10.1103/PhysRevB.102.134408](https://doi.org/10.1103/PhysRevB.102.134408)

## I. INTRODUCTION

The manganese oxides with perovskite structure display a great variety of electronic properties when doped by charge carriers. One of the main issues in the studies of these strongly correlated materials is the ground state emerging from the competition of the antiferromagnetic (AF) superexchange interaction between localized spins and the ferromagnetic (FM) double exchange (DE) interaction of localized spins with itinerant doped carriers.

The lightly electron-doped SrMnO<sub>3-x</sub> compound appears at first as a simple system with no particular physical properties of great current interest. However, as disclosed in the present research, it is the slight oxygen deficiency that gives rise to unusual dynamic correlations of the localized spins due to the competition of the exchange interactions.

The parent manganese oxide SrMnO<sub>3</sub> with the  $Pm\bar{3}m$  crystal structure is a rare example of cubic antiferromagnet. Below  $T_N \approx 240$  K the magnetic moments of Mn<sup>4+</sup> ions ( $^3t_{2g}^0e_g; S = 3/2$ ) are ordered in two sublattices forming a three-dimensional checkerboard pattern of the G-type AF structure with  $\mathbf{q}_{AF} = \pi/a(1, 1, 1)$  [1–3]. Cubic SrMnO<sub>3</sub> has a high Néel temperature and a small magnetic field anisotropy,  $H_a \leq 200$  Oe [4]. A similar situation exists in the well known standard cubic AF RbMnF<sub>3</sub> ( $T_N \approx 83$  K;  $H_a \leq 5$  Oe [5]). In RbMnF<sub>3</sub>, the exchange coupling of the Mn<sup>2+</sup> localized spins

( $^3t_{2g}^2e_g; S = 5/2$ ) is well described within the nearest neighbor only Heisenberg model [6,7] showing the classic isotropic AF properties below  $T_N$  and the Curie-Weiss behavior in the paramagnetic (PM) phase above  $1.3T_N$ . Whereas in nominally stoichiometric SrMnO<sub>3</sub>, the bulk magnetic susceptibility  $\chi$  increases gradually from  $T_N$  reaching a plateau above  $1.5T_N$  with no sign of the mean field behavior [2,8–10]. It follows from an <sup>17</sup>O NMR study of lightly electron-doped SrMnO<sub>3-x</sub> ( $x < 0.01$ ) oxides [4] that this gaplike peculiar behavior of the bulk magnetic susceptibility  $d\chi/dT \geq 0$  should be attributed to the spin susceptibility  $\chi_s$  of the localized spins of Mn ions,  $S(t_{2g})$ .

The gaplike  $T$  dependence of  $\chi$  is typical of compounds with low dimensional AF configuration [6]. It implies that for SrMnO<sub>3</sub>, some short-range magnetic order with a lower-dimensional AF configuration of the  $S(t_{2g})$  spins should add to the main three-dimensional AF–G type configuration. In this configuration, each  $S(t_{2g})$  spin orders antiferromagnetically with its six nearest neighbors [3]. In contrast to RbMnF<sub>3</sub>, in SrMnO<sub>3</sub>, FM correlated pairs of neighboring  $S(t_{2g})$  spins may appear due to the  $t_{2g} - e_g$  electron hopping at empty doubly degenerate  $e_g$  orbital [11]. The broad  $e_g$ -orbital degenerate conduction band,  $W \sim 2$  eV, allows a gain in kinetic energy for the  $e_g$  electrons placing the undoped cubic SrMnO<sub>3</sub> close to the borderline between the metallic and insulating states.

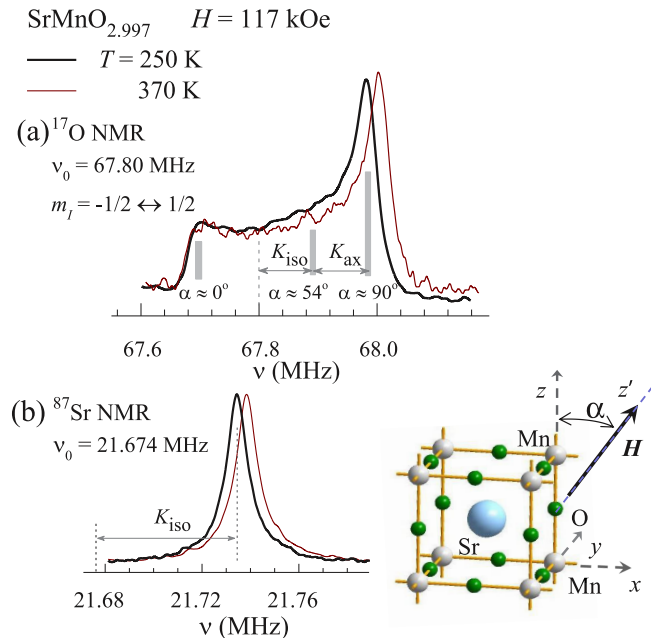


FIG. 1. Paramagnetic phase of polycrystalline cubic  $\text{SrMnO}_{2.997}$  sample. (a) Central line (transition  $m_I = -1/2 \leftrightarrow +1/2$ ) of  $^{17}\text{O}$  NMR spectra and (b)  $^{17}\text{Sr}$  NMR spectra including all the transitions. The angle  $\alpha$  is determined by the direction of the external magnetic field  $\mathbf{H}$  relative to the Mn–O–Mn bond direction.

Furthermore, in lightly  $e$ -doped  $\text{SrMnO}_3$  the energy barrier, separating AF phases with different magnetic unit cell characterized by FM correlated planes (A type [3]) or FM correlated chains (C type [3]) of the  $\text{Mn}^{4+}$  ions is comparable to  $k_B T_N \approx 0.03$  eV [12,13] so that short-wavelength AF phase fluctuations may exist. If these fluctuations exist, they should be enhanced along the path of the diffusing motion of the doped  $e_g$  electrons [14] by the double-exchange mechanism [15]. To our knowledge, there are no studies of low-energy spin excitations in the PM phase because of the absence of large enough  $\text{SrMnO}_3$  single crystals for neutron experiments.

Our recent NMR studies have shown the efficiency of  $^{17}\text{O}$  [4] and  $^{87}\text{Sr}$  [16] NMR probes to investigate the *static* spin correlations of the neighboring  $\text{Mn}^{4+}$  ions in lightly doped  $\text{SrMnO}_{3-x}$ . Some basic results of these NMR studies are used in the present research focusing on the Mn *dynamic* spin correlations in the PM phase of  $\text{SrMnO}_{3-x}$  ( $x < 0.005$ ).

In the perovskite structure, an oxygen atom is directly involved in the formation of both covalent chemical bond and anisotropic superexchange interaction between the localized  $S(t_{2g})$  spins of neighboring Mn. The transferred spin on the  $\text{O}(2p_\pi)$  orbital  $s(2p_\pi) = f_\pi S_z(t_{2g})$ , creates the main contribution,  $^{17}K_{\text{ax}}(2p_\pi)$ , to the anisotropic hyperfine shift of the  $^{17}\text{O}$  NMR line:  $K_{\text{hf}}(\alpha) = K_{\text{ax, hf}}(3 \cos^2 \alpha - 1)$ , where  $\alpha$  is the angle between  $\mathbf{H}$ , the experimental magnetic field and the straight Mn–O–Mn bond (Fig. 1). At  $x \ll 1$  [17],

$$\begin{aligned} ^{17}K_{\text{ax}}(2p_\pi) &= h_{\text{ax}}(2p_\pi)/H \\ &= -4/5\mu_B \langle r^{-3} \rangle_{2p} f_\pi (\langle S_{z1}(t_{2g}) \rangle + \langle S_{z2}(t_{2g}) \rangle)/H \\ &= H(2p_\pi) f_\pi (\langle S_{z1}(t_{2g}) \rangle + \langle S_{z2}(t_{2g}) \rangle)/H, \end{aligned} \quad (1)$$

where  $f_\pi$  is the fractional occupancy of the  $\text{O}(2p_\pi)$  orbital by an unpaired Mn spin and the thermal average  $\langle S_z(t_{2g}) \rangle$  relates to  $\chi_s = g\mu_B \langle S_z(t_{2g}) \rangle / H$ , the local spin susceptibility of  $\text{Mn}^{4+}$  ion, the nearest neighbor of the  $^{17}\text{O}$  probe. A *negative* value  $^{17}K_{\text{ax}}(2p_\pi) < 0$ , following from Eq. (1), defines an asymmetrical shape of the central line (Fig. 1) which intensity is maximum at a higher frequency relative the gravity center,  $^{17}K_{\text{iso}}$ . Whereas the transferred spin on the  $\text{O}(2p_\pi)$  orbital, which lobes are directed along Mn–O–Mn bond, creates a *positive* shift  $^{17}K_{\text{ax}}(2p_\sigma) > 0$ . This shift is negligible in  $\text{SrMnO}_{3-x}$  ( $x \ll 1$ ) because of the almost zero occupancy of the Mn( $e_g$ ) orbital, Mn( $e_g$ ) being the counterpart in Mn( $e_g$ )–O( $2p_\sigma$ ) covalency (Eqs. (5) and (6) in Ref. [4]). Thus the temperature dependence of  $|K_{\text{ax}}|$  is the one of  $\chi_s(T)$ .<sup>1</sup>

The isotropic component of the hyperfine magnetic shift  $^{17}K_{\text{iso}}$  arises *only in doped*  $\text{SrMnO}_{3-x}$ . It is due to the Fermi contact interaction of the nuclear spin  $^{17}I$  with spin density  $s_z(2s) = f_{2s} s_z(e_g) = f_{2s} n_{e_g} J / E_F \langle S_z(t_{2g}) \rangle$ , created by the  $n_{e_g}$  fast-moving doped electrons, with  $n_{e_g} \leq 2x$ . The  $n_{e_g}$  electrons become itinerant in the conduction band  $\text{O}(2s)$ –Mn( $e_g$ ), having a dominant  $e_g$  character [14,18]. Because of the strong intra-atomic exchange interaction with the almost localized  $t_{2g}$  electrons,  $-J_s(e_g)S(t_{2g})$ , the band consists of spin-up polarized states with the density of states  $g(E_F) \sim n_{e_g}/E_F$  when  $x \ll 1$  [12], and

$$\begin{aligned} ^{17}K_{\text{iso}} &= ^{17}h(e_g)/H \\ &= H_{\text{FC}}(2s) f_{2s} (J_H/E_F) n_{e_g} (\langle S_{z1}(t_{2g}) \rangle + \langle S_{z2}(t_{2g}) \rangle)/H \\ &= ^{17}H(e_g) n_{e_g} (\langle S_{z1}(t_{2g}) \rangle + \langle S_{z2}(t_{2g}) \rangle)/H. \end{aligned} \quad (2)$$

Here, the hyperfine magnetic field,  $H_{\text{FC}}(2s)$ , is created by one unpaired electron residing at the  $\text{O}(2s)$  orbital. According to Eqs. (1) and (2), the ratio  $K_{\text{iso}}(T)/|K_{\text{ax}}|$  is proportional to  $n_{e_g}/2x$ , the fraction of the fast-moving doped electrons per Mn. Only these fast-moving  $n_{e_g}$  electrons provide the  $^{17}\text{O}$  NMR shift,  $^{17}K_{\text{iso}}$ , defined by Eq. (2).

The same reasoning is valid for  $^{17}\text{Sr}$  NMR. In  $\text{SrMnO}_3$  the Sr atom has eight nearest Mn neighbors. The corresponding isotropic hyperfine shift,  $^{87}K_{\text{iso}}$ , is caused by the spin densities  $s_z(5s) = f_{5s} s_z(e_g) = f_{5s} n_{e_g} J / E_F \langle S_{z,i}(t_{2g}) \rangle$ , transferred to the Sr( $5s$ ) orbital by each magnetic neighbor:

$$\begin{aligned} ^{87}K_s &= ^{87}h(e_g)/H \\ &= H_{\text{FC}}(5s) f_{5s} (J/E_F) n_{e_g} \sum_i \langle S_{z,i}(t_{2g}) \rangle / H \\ &= ^{87}H(e_g) n_{e_g} \sum_i \langle S_{z,i}(t_{2g}) \rangle / H. \end{aligned} \quad (3)$$

In addition, it was shown that in the AF ordered phase at low temperature, all doped electrons have slowed down the Mn–Mn hopping. In this situation, there is an increase of FM interaction between Mn neighbors by means of the DE mechanism [19] leading to the formation of small-size magnetic polarons in the G-type AF matrix. These polarons were detected below 10 K by  $^{55}\text{Mn}$  NMR [4].

<sup>1</sup>In  $\text{SrMnO}_3$ , the contribution  $K_{\text{ax,dip}}$  of the classic dipolar fields from neighboring induced  $\text{Mn}^{4+}$  moments  $m_{z||H}(\text{Mn}) = \chi_{\text{mol}} H / N_A$  is about three time smaller than  $|^{17}K_{\text{ax}}(2p_\pi)|$  [4]. Thus the value of  $^{17}K_{\text{ax}}(2p_\pi)$  was obtained in the following way:  $^{17}K_{\text{ax}}(2p_\pi) = K_{\text{ax,measured}} - K_{\text{ax,dip}}$ .

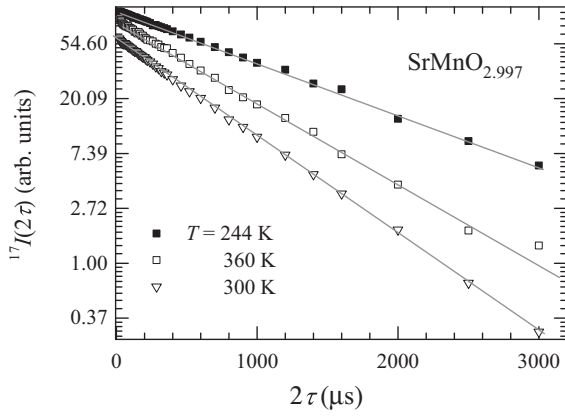


FIG. 2. Integral of the spectral intensity  $^{17}I(2\tau)$  of the  $^{17}\text{O}$  NMR central line at  $\alpha \approx 54^\circ$  as a function of  $2\tau$  (see text). The solid lines are the fit with a single exponential decay  $^{17}I_\alpha(2\tau) \propto \exp(-2\tau/^{17}T_2)$ .

In this paper, we study the time-dependent part of the hyperfine fields  $^{17}h(e_g)$ ,  $^{87}h(e_g)$ , and  $^{17}h(2p_\pi)$  at low frequencies by measuring the spin-lattice relaxation rate  $T_1^{-1}$  and the spin-echo decay rate  $T_2^{-1}$  of  $^{17}\text{O}$  and  $^{17}\text{Sr}$  nuclei. The results shed light on the slow-fluctuating short-range correlations between the localized Mn spins,  $S(t_{2g})$ , in the PM phase of a lightly electron doped cubic  $\text{SrMnO}_{3-x}$  polycrystalline sample, i.e.,  $\text{SrMnO}_{2.997}$  ( $x < 0.005$ ). A description of the short-range magnetic orders is inferred.

## II. EXPERIMENTAL DETAILS

The  $\text{SrMnO}_{2.997}$  polycrystalline sample with the cubic structure was synthesized following the procedure described in Ref. [4]. At the last stage of synthesis the sample was annealed during 24 hours at  $T = 500^\circ\text{C}$  in oxygen flow ( $P_{\text{O}_2} = 1$  bar) containing 70% of  $^{17}\text{O}$  isotope, for  $^{17}\text{O}$  NMR measurements. According to x-ray diffraction the  $^{17}\text{O}$ -enriched sample has the  $Pm\bar{3}m$  perovskite structure with the unit cell parameter  $a = 3.8062(4)$  Å at room temperature. In order to estimate the oxygen content of our sample,  $3 - x = 2.997$ , we used a phenomenological dependence law of the lattice cell parameter versus the oxygen deficiency,  $a(x)$ , which was suggested in Ref. [4] for cubic  $\text{SrMnO}_{3-x}$  compounds with  $x < 0.01$ . Let us note that a slightly less doped  $^{17}\text{O}$ -enriched sample,  $\text{SrMnO}_{2.998}$ , was described in Ref. [4]. We use their  $^{17}T_2$  data at room temperature in Sec. III C.

Magnetization measurements were carried out with a magnetometer PPMS-9 (Quantum Design) on cooling the sample in magnetic field  $H = 90$  kOe. The corresponding dc magnetic susceptibility  $\chi = M/H$  demonstrates a plateaulike behavior in a broad temperature range above  $T_N = 236(2)$  K with no signature of the Curie-Weiss law dependence [Fig. 3(a)].

The  $^{17}\text{O}$  and  $^{17}\text{Sr}$  NMR measurements were performed with AVANCE II(III) – 500WB (Bruker) NMR spectrometer in the temperature range 200 – 400 K and  $H = 117$  kOe. The broad NMR spectra of both,  $^{17}\text{O}$  (spin  $^{17}I = 5/2$ ) and  $^{17}\text{Sr}$  ( $^{87}I = 9/2$ ) nuclei (Fig. 1) were obtained by summing the Fourier-transformed half-echo signals acquired at

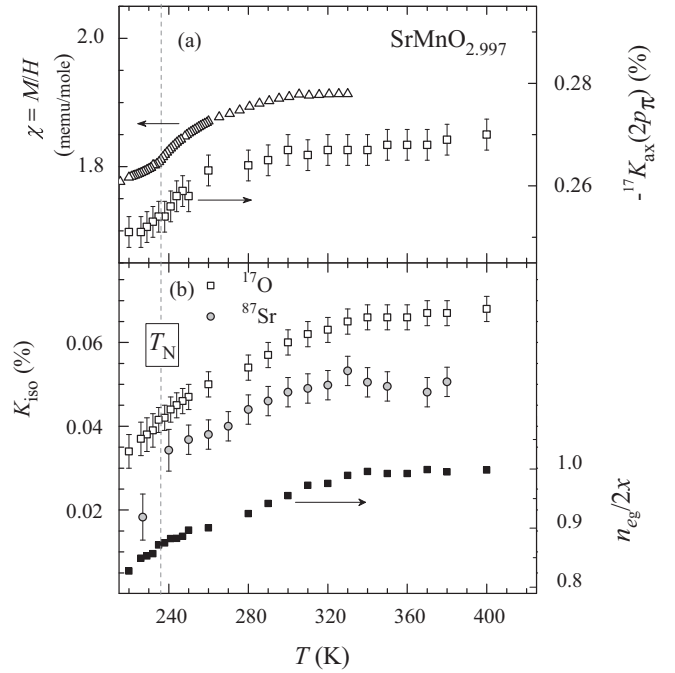


FIG. 3. Temperature dependence of (a) the bulk magnetic susceptibility  $\chi = M/H$ ; the axial hyperfine component  $^{17}K_{\text{ax}}(2p_\pi)$  of the  $^{17}\text{O}$  NMR shift, and (b) isotropic hyperfine NMR shift  $K_{\text{iso}}$  of both nuclei  $^{17}\text{O}$  and  $^{17}\text{Sr}$ ;  $n_{\text{eq}}/2x$  is the fraction per Mn atom of the fast-moving doped electrons.

equidistant (80 KHz) operating frequencies. The  $^{17}\text{O}$  ( $^{17}\text{Sr}$ ) NMR shifts  $^{17(87)}K$  are defined relative to the Larmor frequency  $^{17}\nu_0 = 67.80$  MHz ( $^{87}\nu_0 = 21.67$  MHz),  $^{17(87)}K = (\nu - ^{17(87)}\nu_0) / ^{17(87)}\nu_0$ .

The spin-lattice relaxation rate of  $^{17}\text{O}$  nuclei  $^{17}T_1^{-1}$  was measured on the central line of the  $^{17}\text{O}$  NMR spectrum (Fig. 1) by the inversion-recovery technique using the pulse sequence  $2p-t_{\text{inv}}-p-\tau-p-\tau$ -echo signal  $^{17}E(t_{\text{inv}})$  with fixed delay  $\tau = 30$   $\mu\text{s}$ , variable  $t_{\text{inv}} = 0.01$ –250 ms and a pulse duration  $p = 1.6$   $\mu\text{s}$ . At each  $t_{\text{inv}}$ , the integral of spectral intensity of the line  $I_\alpha(t_{\text{inv}})$  taken in the frequency range  $\nu_\alpha \pm 0.005$  MHz was measured, where  $\nu_\alpha$  corresponds to the angle  $\alpha$ . At  $\alpha_{\text{magic}} = \arccos(1/\sqrt{3}) = 54.7^\circ$ , all nuclear  $m_I$  levels of  $^{17}\text{O}$  are equidistant so that the  $\{I_\alpha(t_{\text{inv}})\}$  data array is well described by a single-exponential dependence [20]:  $(I_{\alpha,0} - I_\alpha(t_{\text{inv}})) \propto \exp(-t_{\text{inv}}/^{17}T_1)$ , where  $I_{\alpha,0} = I_\alpha(t_{\text{inv}})$  at  $t_{\text{inv}} \geq 5T_1$ . The rate  $^{17}T_1^{-1}$  was determined also at  $\alpha = 40^\circ$  and  $70^\circ$  aiming to evaluate the anisotropic contribution  $^{17}T_1^{-1}(2p_\pi) \propto (2 + 3\sin^2\alpha)$  of the fluctuating hyperfine field  $h_{\text{ax}}(2p_\pi)$ . The value of  $^{17}T_1$  was approximated by a single-exponential fit of  $\{I_\alpha(t_{\text{inv}})\}$  raw data in the range  $0.5T_1 \leq t_{\text{inv}} \leq 5T_1$ .

For  $^{17}\text{Sr}$  nuclei, the spin-lattice relaxation rate  $^{87}T_1^{-1}$  was measured at the peak of the spectrum (Fig. 1) using the pulse sequence  $p-\tau-p-\tau$ -echo signal  $^{87}E(2\tau, t)$  with fixed  $\tau = 100$   $\mu\text{s}$ ,  $p = 3$   $\mu\text{s}$  and variable repetition time of the pulse sequence,  $t = 0.005$ –2 s. Over the entire temperature range the excitation bandwidth [21]  $(\delta\nu)_{\text{BW}} = 2.8/\pi p = 300$  KHz is three times larger than the width of the  $^{17}\text{Sr}$  NMR spectra which includes all  $2 \times ^{87}I = 9$  transitions. Indeed, the NMR spectrum of the quadrupolar nuclei  $^{17}\text{Sr}$  ( $^{87}Q = 0.15$  barn)

has no quadrupolar splitting due to the cubic symmetry, in average, of the  $^{17}\text{Sr}$  electrical environment as shown in Fig. 1. Because of that, the method for measuring  $^{87}\text{T}_1$  yields a single exponential recovery.

The spin-echo decay rate  $T_2^{-1}$  of  $^{17}\text{O}$  and  $^{17}\text{Sr}$  nuclei were measured using the pulse sequence  $p\text{-}\tau\text{-}2p\text{-}\tau\text{-}$ echo signal  $E(2\tau)$ , with  $p(^{17}\text{O}) = 1.6 \mu\text{s}$ ;  $p(^{87}\text{Sr}) = 3 \mu\text{s}$ . For  $^{17}\text{Sr}$  nuclei, the measurements were performed at the peak of the  $^{17}\text{Sr}$  NMR spectrum. The intensity of the echo signal  $I(2\tau)$  was acquired as a function of  $\tau$ , the delay between the pulses. The  $^{87}\text{T}_2$  value was determined by fitting of the  $\{^{87}I(2\tau)\}$  data array with the expression  $^{87}I(2\tau) = I(0)\exp(-2\tau/^{87}\text{T}_2)$ . For  $^{17}\text{O}$  nuclei, the integral of the spectral intensity of the central line  $^{17}I_\alpha(2\tau) \propto ^{17}E_\alpha(2\tau)$  was considered. This integral was measured in the frequency range  $\nu_\alpha \pm 0.005 \text{ MHz}$  and as a function of  $2\tau$ , at fixed  $\nu_\alpha$ , where  $\nu_\alpha$  corresponds to the angle  $\alpha$ . Some representative  $^{17}I_\alpha(2\tau)$  raw data collected at  $\alpha_{\text{magic}} = 54.7^\circ$  and at different temperatures are plotted in a semilogarithmic scale in Fig. 2. As can be seen on the figure the drop of the echo signal  $^{17}I_\alpha(2\tau)$  on more than  $e^3$  times is well described by a single exponential dependence over the entire temperature range.

### III. RESULTS AND DISCUSSION

#### A. Static spin susceptibility traced by $^{17}\text{O}$ and $^{87}\text{Sr}$ NMR shift

Figure 1 shows at  $T = 250$  and  $370 \text{ K}$  the central line (transition  $m_I = -1/2 \leftrightarrow +1/2$ ) of the  $^{17}\text{O}$  NMR and the  $^{17}\text{Sr}$  NMR spectra which include all the  $2 \times I = 9$  transitions. For both probe nuclei, the spectra are shifted toward higher frequencies relative to the corresponding Larmor frequency  $^{17(87)}\nu_0$  so that the hyperfine isotropic shifts  $^{17(87)}K_{\text{iso}}$  are positive; their growth with  $T$  is shown in Fig. 3(b).

(1) The growth with temperature of the hyperfine axial shift  $|^{17}K_{\text{ax}}(2p_\pi)| \propto \chi_s$  confirms the gaplike  $d\chi_s/dT \geq 0$  behavior of static spin susceptibility of the localized  $S(t_{2g})$  spins in the PM phase of  $\text{SrMnO}_{2.997}$  [Fig. 3(a)].

(2) Below  $350 \text{ K}$  the ratio  $|^{17}K_{\text{iso}}(T)|/|^{17}K_{\text{ax}}(T)|$  decreases. As it is proportional to  $n_{e_g}$ , the number of fast-moving doped electrons, the decrease indicates that the number of slow-moving electrons ( $2x - n_{e_g}$ ) grows [Fig. 3(b)]. These doped electrons slow down their rate of Mn–Mn hopping, thus locally enhancing the FM interaction of their Mn neighbors by means of the DE mechanism [19]. With decreasing  $T$  the time  $\tau$  during which such electrons are near Mn ions, increases following the Arrhenius law  $\tau(T) \propto \exp(E_a/T)$  where the energy barrier  $E_a$  is about  $300 \text{ K}$ . Below  $50 \text{ K}$  when  $\tau \geq 6 \times 10^{-9} \text{ s}$ , these slow-moving electrons create static FM nanodomains.

(3) In the PM phase, the slow-moving ( $2x - n_{e_g}$ ) electrons create along their diffusion path the local field  $h_{\text{FM}}$ , which is far larger than the  $h(e_g)$  value defined by Eqs. (2) and (3). So that during the time  $\tau \ll 2\pi/\omega_0$ , the local field  $h_{\text{FM}}$  shifts the resonance frequency of the  $^{17(87)}I$  neighbors out of the NMR window studied in this work and shown in Fig. 1. Consequently, and as it is observed, no static magnetic broadening of the  $^{17(87)}\text{NMR}$  spectra should occur when  $T$  decreases. These pulselike fluctuations of the local field, caused

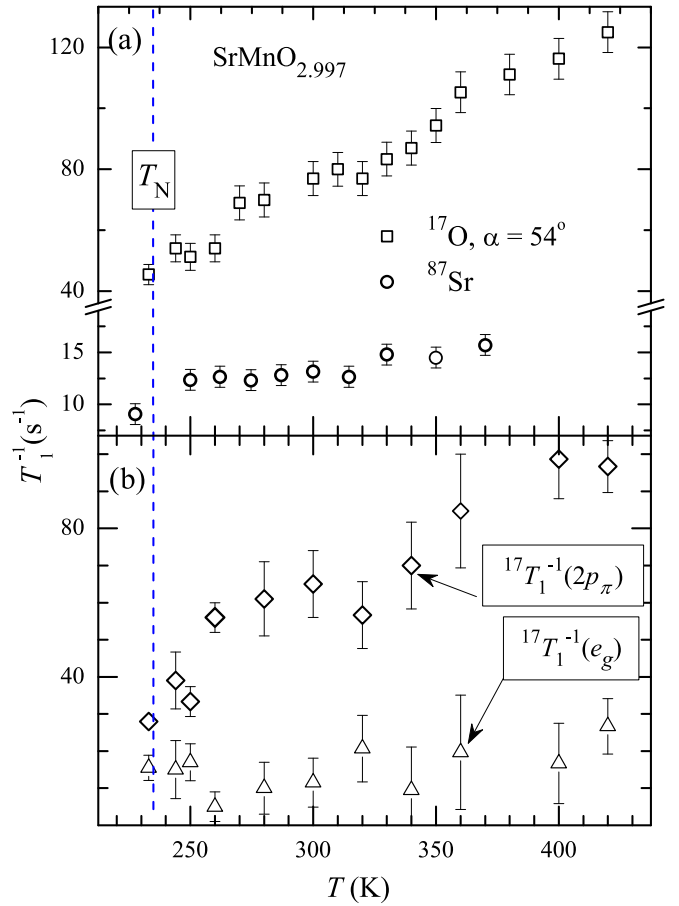


FIG. 4. Temperature dependence of (a) the spin-lattice relaxation rate  $T_1^{-1}$  of  $^{17}\text{O}$  ( $\alpha = 54^\circ$ ) and  $^{87}\text{Sr}$  nuclei, and (b) isotropic  $^{17}\text{T}_1^{-1}(e_g)$  and anisotropic  $^{17}\text{T}_1^{-1}(2p_\pi)$  contributions to  $^{17}\text{T}_1^{-1}$  at  $\alpha = 54^\circ$ .

by slow-moving ( $2x - n_{e_g}$ ) electrons, may have an impact on the nuclear spin relaxation of both NMR probes as explained below.

#### B. Spin-lattice relaxation of $^{17}\text{O}$ and $^{17}\text{Sr}$ nuclei

Figure 4(a) shows the thermal behavior of the spin-lattice relaxation rate  $T_1^{-1}$  of  $^{17}\text{O}$  ( $\alpha = 54^\circ$ ) and  $^{17}\text{Sr}$  nuclei. Above  $T_N$ , both rates  $^{17}\text{T}_1^{-1}$  and  $^{87}\text{T}_1^{-1}$  are roughly proportional to  $T$ .

Let us consider  $^{17}\text{T}_1^{-1}(\alpha, T)$ . According to Eqs. (1) and (2), its value is contributed by the time fluctuating part of the isotropic hyperfine field  $h(e_g)$ ,  $^{17}\text{T}_1^{-1}(e_g)$ , and of the  $\alpha$ -dependent hyperfine field  $h(2p_\pi)$  with  $^{17}\text{T}_1^{-1}(2p_\pi) \propto (2 + 3 \sin^2 \alpha)$  [22]:

$$^{17}\text{T}_1^{-1}(\alpha) = ^{17}\text{T}_1^{-1}(2p_\pi) + ^{17}\text{T}_1^{-1}(e_g). \quad (4)$$

More precisely,  $^{17}\text{T}_1^{-1}(2p_\pi)$  is due to the time dependence of the transverse component  $h_\perp(2p_\pi)$ , which originates from the fluctuations at the frequency  $\omega = ^{17}\gamma H$  of the transverse  $S_{i,x'(y')}$  components of the localized  $S(t_{2g})$  spins of neighboring  $\text{Mn}^{4+}$  ions through the corresponding spin transfer  $s_{x'(y')}(2p_\pi) = f_\pi S_{x'(y')}(t_{2g})$  on the  $\text{O}(2p_\pi)$  orbital [23]. The transverse component  $h_\perp(2p_\pi)$  of the hyperfine field  $h(2p_\pi)$  lies in the  $x'y'$  plane orthogonal to  $\mathbf{H} \parallel \mathbf{z}'$  and is defined as  $h_\perp(2p_\pi) = H(2p_\pi)f_\pi\{S_{1,x'(y')}(t_{2g}) + S_{2,x'(y')}(t_{2g})\}$ . These two

contributions to  $^{17}T_1^{-1}(\alpha)$ , having different  $\alpha$  dependencies, were separated from each other by measuring the rate  $^{17}T_1^{-1}$  at  $\alpha = 40^\circ$ ,  $54^\circ$ , and  $70^\circ$ . As seen on Fig. 4, the magnitude and  $T$  dependence of  $^{17}T_1^{-1}$  are determined by  $^{17}T_1^{-1}(2p_\pi)$ .

$$^{17}T_1^{-1}(2p_\pi) = \frac{\gamma^2 k_B}{16\mu_B^2} (H(2p_\pi)f_\pi)^2 T (2 + 3 \sin^2 \alpha) \times \sum_q \cos^2(q_z a/2) \chi_s''(q, \omega)/\omega. \quad (5a)$$

The factor  $(2 + 3 \sin^2 \alpha)$  takes into account the  $\alpha$  dependence of  $^{17}T_1^{-1}(2p_\pi)$ ,  $\chi_s''(q, \omega) \propto \int_0^\infty d\tau (S_q(\tau)S_q(0)) \cos(\omega\tau)$  is the imaginary part of the dynamic spin susceptibility. Its value determines the spectral intensity of the  $q$  component of the correlation function of the fluctuating neighboring  $S(t_{2g}, t)$  spins at the frequency  $\omega$ . Because the  $^{17}T_1^{-1}$  data were obtained at  $\omega_{\text{NMR}} \ll \omega_{\text{ex}}$  where  $\omega_{\text{NMR}} = ^{17}\gamma H = 4 \times 10^8 \text{ s}^{-1}$  and  $\omega_{\text{ex}} \approx 5.8 \times 10^{12} \text{ s}^{-1}$  Ref. [13], we may approximate  $\chi_s''(q, \omega)/\omega \approx \chi_s'(q)/\omega_{\text{sf}}$ . Furthermore, the long-wavelength terms with  $q \ll \pi/a$  are the only significant terms in the summation of Eq. (5) because of the specific  $q$  dependence of the form-factor. After reducing  $\sum_q \cos^2(q_z a/2) \chi_s''(q, \omega)/\omega \rightarrow \sum_{q \sim 0} \chi_s'(q)/\omega_{\text{sf}}(q) \rightarrow \chi_s(q=0)/\omega_{\text{sf}}$ , Eq. (5) takes the final form:

$$^{17}T_1^{-1}(2p_\pi) = \frac{\gamma^2 k_B}{16\mu_B^2} (H(2p_\pi)f_\pi)^2 \times T (2 + 3 \sin^2 \alpha) \chi_s(q=0)/\omega_{\text{sf}}, \quad (5b)$$

where  $\chi_s(q=0)$  is the uniform ( $q=0$ ) spin susceptibility of the localized  $S(t_{2g})$  spins. The almost  $T$ -independent behavior of  $\chi_s(q=0)$  is well traced by static  $^{17}\text{O}$  NMR data.

The linear growth with  $T$  of  $^{17}T_1^{-1}(2p_\pi)$  indicates an almost  $T$ -independent value of  $\hbar\omega_{\text{sf}}$ , the characteristic energy of the damped magnon excitations, at  $q \ll \pi/a$  of AF coupled  $S(t_{2g})$  spins in the PM phase of  $\text{SrMnO}_{2.997}$  with  $\hbar\omega_{\text{sf}} = 2.5(7) \text{ meV}$ .<sup>2</sup> This value is about 1.5 times less than the exchange energy  $\hbar\omega_{\text{ex}}(q = \pi/a) = 3.8(2) \text{ meV}$ , i.e.,  $5.8(1) \times 10^{12} \text{ s}^{-1}$ , estimated at  $T_N = 236 \text{ K}$ . In a classic AF scenario, just above  $T_N$  a peak of  $\chi_s(q)$  at  $q \sim \pi/a$  is expected; as  $T$  increases in the PM phase, this peak is more or less smeared out so that  $\chi_s(q)$  at  $q \sim q_{\text{AF}}$  decreases while  $\chi_s(q)$  at  $q \sim 0$  increases. That is why the  $T$ -independent behavior of the  $\chi_s(q)/\omega_{\text{sf}}(q)$  ratio at  $q \sim 0$  is unexpected; it could imply that even far above  $T_N$  some peak of  $\chi_s(q)$  at  $q \sim q_{\text{AF}}$  would still exist. Thus the  $^{17}T_1^{-1}$  results indirectly indicate a high thermal stability of the fluctuating short-range magnetic order (SRMO) in the PM phase of  $\text{SrMnO}_{2.997}$ , unlike  $\text{RbMnO}_3$ , where a thermally fragile SRMO was observed only up to  $1.1T_N$  in inelastic neutron scattering experiments [24].

As seen in Fig. 4, the increase with  $T$  of  $^{17}T_1^{-1}(e_g)$  and  $^{87}T_1^{-1}$  is less pronounced than for  $^{17}T_1^{-1}(2p_\pi)$ . According to Eqs. (2) and (3) their values are defined by the spectral intensity, built at  $^{17(87)}\omega_{\text{NMR}}$  by the product of two correlation functions:  $\langle n_{e_g}(t)n_{e_g}(0) \rangle$  relevant to the fast moving doped

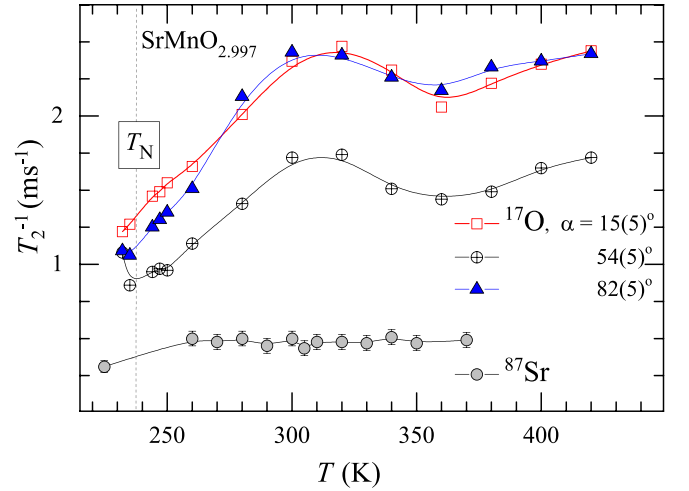


FIG. 5. Thermal behavior of  $^{17}\text{O}$  and  $^{17}\text{Sr}$  spin-echo decay rates in  $\text{SrMnO}_{2.997}$ . The angle  $\alpha$  defines the direction of the magnetic field  $\mathbf{H}$  relative to the Mn–O–Mn bond direction. The solid curves are guide for the eye.

$e_g$  electrons and  $\langle S_q(t)S_q(0) \rangle$  of the localized  $S(t_{2g})$  spins. The small variation of  $^{17}T_1^{-1}(e_g)$  and  $^{87}T_1^{-1}$  (Fig. 4) shows that, in the frequency range  $^{17(87)}\omega_{\text{NMR}} = (1-4) \times 10^8 \text{ s}^{-1}$ , the spectral intensity is not much influenced by  $\langle n_{e_g}(t)n_{e_g}(0) \rangle$ . In contrast, at very low frequencies  $\langle n_{e_g}(t)n_{e_g}(0) \rangle$  leads to an abnormal growth of the fluctuating  $^{17}h(e_g)$ , as seen below.

### C. $^{17}\text{O}$ and $^{87}\text{Sr}$ spin-echo decay rate

The thermal behavior of the spin-echo decay rates are shown on Fig. 5. Unlike the almost constant value of  $^{87}T_2^{-1}$ , the  $^{17}T_2^{-1}$  rate increases with  $T$  passing through a broad peak around  $T = 310 \text{ K}$ , whatever the value of the angle  $\alpha$ .

Compared to  $^{17(87)}T_1^{-1}$  which is only proportional to  $h_\perp^2$ , the spin-echo decay rate is determined by both time-dependent components:  $h_\perp \perp \mathbf{H}$  at  $\omega = ^{17(87)}\omega_{\text{NMR}}$  and  $h_\parallel \parallel \mathbf{H}$  at much lower frequency,  $\omega \leq 10^3 \text{ s}^{-1}$ , of the corresponding hyperfine fields  $^{17}h(2p_\pi)$ ,  $^{17}h(e_g)$ , and  $^{87}h(e_g)$  [23]:

$$^{17(87)}T_2^{-1} = ^{17(87)}T_2^{-1}(h_\parallel) + ^{17(87)}(T_{1,\text{echo}}(h_\perp))^{-1}. \quad (6)$$

The contribution  $(T_{1,\text{echo}})^{-1}$  in Eq. (6) is enhanced compared to the corresponding spin-lattice relaxation rate  $T_1^{-1}$ . As Eqs. (6a) and (6b) show, the enhancement depends on the fluctuating local field. For  $^{17}\text{Sr}$  nuclei, it is

$$^{87}(T_{1,\text{echo}})^{-1} = (^{87}I + 1/2)^2 (^{87}T_1(e_g))^{-1}. \quad (6a)$$

For  $^{17}\text{O}$  nuclei, the second term in Eq. (6) depends on  $\alpha$  [25,26]. Compared with previous  $^{17}T_2^{-1}$  consideration presented in Ref. [4] at room temperature for the less doped  $\text{SrMnO}_{2.998}$ , we use here an expression for the  $^{17}T_{1,\text{echo}}(h_\perp)^{-1}$  rate taking into account both an isotropic contribution of doped electrons,  $^{87}T_1(e_g)^{-1}$ , and anisotropic contribution of localized  $S(t_{2g})$  spins,  $^{17}T_1^{-1}(2p_\pi)$ :

$$(^{17}T_{1,\text{echo}})^{-1} = (^{17}I + 1/2)^2 (^{17}T_1(e_g))^{-1} + (5.25 + 5.625 \sin^2 \alpha) (^{17}T_1(2p_\pi, \alpha = 54^\circ))^{-1}, \quad (6b)$$

<sup>2</sup>The  $\omega_{\text{sf}}$  ( $q \ll \pi/a$ ) value was estimated using Eq. (5a) with the  $^{17}T_1^{-1}(2p_\pi)$  rate in Fig. 4(b) and the product  $H(2p_\pi)f_\pi = 7 \text{ kOe}$  deduced from Eq. (1) and the  $^{17}K_{\text{ax}}$  and  $\chi = M/H$  data in Fig. 3.

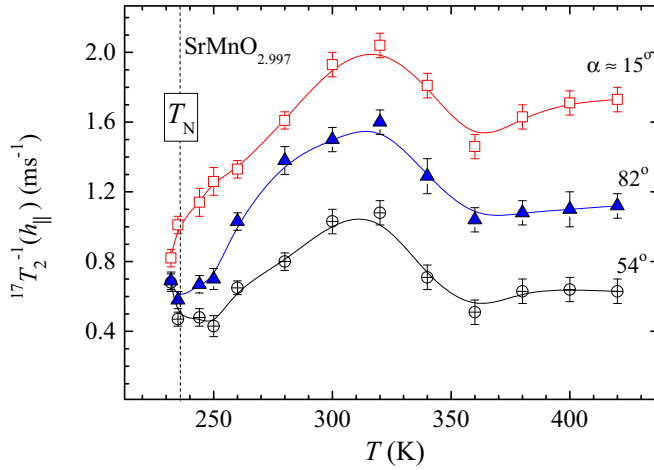


FIG. 6. Temperature dependence of  $^{17}T_2^{-1}(h_{\parallel})$  for different values of the angle  $\alpha$ .

where the  $(^{17}T_1(e_g))^{-1}$  and  $^{17}T_1^{-1}(2p_{\pi}, \alpha = 54^\circ)$  values are shown at each temperature in Fig. 4. For both nuclei,  $(T_{1,\text{echo}})^{-1}$  varies monotonically with temperature. By subtracting these terms from the measured data  $(T_2^{-1})_{\text{exp}}$ , the spin-echo decay rate  $T_2^{-1}(h_{\parallel})$  defined by the fluctuations of  $h_{\parallel}$  is obtained:

$$\begin{aligned} ^{17}T_2^{-1}(h_{\parallel}) &= (T_2^{-1})_{\text{exp}} - (T_{1,\text{echo}})^{-1} \\ &= ^{17}T_{2,e_g}^{-1}(h_{\parallel}) + ^{17}T_{2,2p_{\pi}}^{-1}(h_{\parallel}). \end{aligned} \quad (7)$$

Figure 6 shows the  $T$  dependence of  $^{17}T_2^{-1}(h_{\parallel})$  for  $\alpha = 15^\circ$ ,  $54^\circ$ , and  $82^\circ$ . The two terms in Eq. (7) are due to the isotropic fluctuations of the hyperfine field  $^{17}h(e_g)$  and anisotropic fluctuations of the hyperfine field  $^{17}h(2p_{\pi}) \propto (1 - 3 \cos^2 \alpha)$ , respectively. Let us consider the  $\alpha$  dependence of  $^{17}T_2^{-1}(h_{\parallel})$ . Figure 7 shows  $^{17}T_2^{-1}(h_{\parallel})$  as a function of the angle  $\alpha$  for  $\text{SrMnO}_{2.997}$  ( $x = 0.003$ ) at  $T = 244$  and  $420$  K, and for the less doped  $\text{SrMnO}_{2.998}$  ( $x = 0.002$ ) [4] at  $T = 300$  K. At each temperature the  $\{^{17}T_2^{-1}(h_{\parallel})\}$  data array was fitted with the expression  $a + b(1 - 3 \cos^2 \alpha)^2$  aiming to determine both the isotropic  $^{17}T_{2,e_g}^{-1}(h_{\parallel}) \equiv a$  and anisotropic  $^{17}T_{2,2p_{\pi}}^{-1}(h_{\parallel}) \equiv b(1 - 3 \cos^2 \alpha)^2$  contributions. Their temperature dependencies are shown in Fig. 8.

Comparing  $\text{SrMnO}_{2.997}$  to the less doped  $\text{SrMnO}_{2.998}$  sample, the value of  $^{17}T_{2,2p_{\pi}}^{-1}(h_{\parallel})$  is not changed, unlike the contribution  $^{17}T_{2,e_g}^{-1}(h_{\parallel})$ , as seen on Fig. 8(a). As  $^{17}T_{2,2p_{\pi}}^{-1}(h_{\parallel})$  shows no dependence on  $x$ , it is expected to be the same in the stoichiometric ( $x = 0$ )  $\text{SrMnO}_3$ , where  $^{17}T_{2,2p_{\pi}}^{-1}(h_{\parallel})$  is caused by fast fluctuations ( $\omega_{\text{ex}} \gg ^{17}\omega_0$ ) of the exchange-coupled localized  $S(t_{2g})$  spins. In the scenario of the nearest-neighbor AF exchange interaction, the spins  $S_1, S_2$  of the two neighboring Mn1, Mn2 spend all the time in the ground singlet state ( $S_1 + S_2 = 0$ ). The local field  $h_{\parallel}(t)$  created by these spins at oxygen has no vanishing mean square value  $\langle (h_{\parallel,\text{singlet}})^2 \rangle \sim (^{17}K_{\text{hf,ax}}H)^2$ . As for  $^{17}\omega_0/\omega_{\text{ex}} \ll 1$ , the rate  $^{17}T_{2,2p_{\pi}}^{-1}(h_{\parallel})$  can be written as  $\gamma^2 \langle (h_{\parallel,\text{singlet}})^2 \rangle \times 2\pi/\omega_{\text{ex}}$  [23],  $^{17}T_2^{-1}(h_{\parallel})$  is thus estimated to be  $0.5 \text{ s}^{-1}$ . This value is far smaller

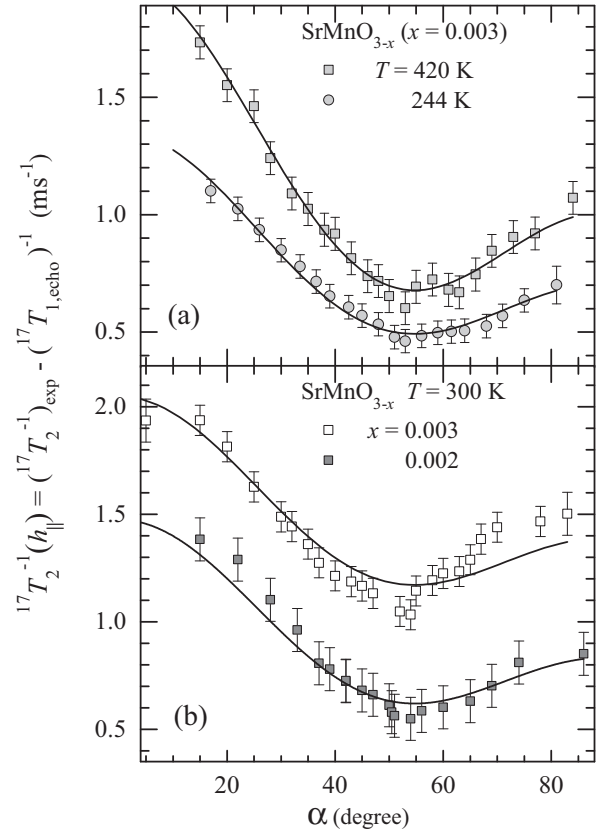


FIG. 7.  $^{17}\text{O}$  spin-echo decay rate  $^{17}T_2^{-1}(h_{\parallel})$  vs  $\alpha$  in (a)  $\text{SrMnO}_{2.997}$  at  $T = 244$  and  $420$  K and (b) in  $\text{SrMnO}_{2.997}$  and  $\text{SrMnO}_{2.998}$  at  $T = 300$  K. The solid curves are the fits with the expression  $a + b(1 - 3 \cos^2 \alpha)^2$ .

than the experimental rate  $^{17}T_2^{-1}(h_{\parallel}) = 0.2\text{--}0.3 \text{ ms}^{-1}$  shown on Fig. 8(b).

The large experimental value of  $^{17}T_2^{-1}(h_{\parallel})$  is most likely due to an increase of  $\langle (h_{\parallel})^2 \rangle$ , created at oxygen by the neighboring  $S(t_{2g})$  spins,  $S_1, S_2$ , which instant configuration is not only the ground state but also the excited triplet state ( $S_1 + S_2 = 2S$ ) with  $h_{\parallel,\text{triplet}} \gg h_{\parallel}$ . During the time  $\tau_{\text{singlet}}$ , the  $^{17}\text{O}$  resonance frequency,  $\nu_{\text{singlet}} = \gamma h_{\parallel,\text{singlet}}$ , it is about  $0.1 \text{ MHz}$  whereas during the time  $\tau_{\text{triplet}}$ ,  $\nu_{\text{triplet}} = \gamma h_{\parallel,\text{triplet}}$  it is about  $25 \text{ MHz}$  [27]. The latter frequency value is far above our experimental NMR window in Fig. 1. The ratio  $\tau_{\text{triplet}}/\tau_{\text{singlet}}$  is equal to  $P_{\text{triplet}}/P_{\text{singlet}}$ , the ratio of the probabilities to find the Mn neighbors in the triplet or singlet configurations. At  $\tau_{\text{triplet}}/\tau_{\text{singlet}} \ll 1$  and for  $^{17}T_{2,2p_{\pi}}^{-1}(h_{\parallel}) = (\gamma h_{\parallel,\text{triplet}} P_{\text{triplet}}/P_{\text{singlet}})^2 > 2\pi/\omega_{\text{ex}}$  [28,29] we get at room temperature the ratio  $P_{\text{triplet}}/P_{\text{singlet}} = 0.08$ . This value quantifies the proportion of FM and AF correlated  $S(t_{2g})$  spin pairs which exist at room temperature in the PM phase of slightly electron doped as well as in *undoped* cubic  $\text{SrMnO}_3$ .

Let us now turn to  $^{17}\text{O}$  and  $^{17}\text{Sr}$   $T_{2,e_g}^{-1}(h_{\parallel})$  rates defined by the time fluctuating component along  $H$ ,  $h_{\text{hf},\parallel}(e_g)$ , of the hyperfine fields  $h_{\text{hf}}(e_g)$ , where  $h_{\text{hf},\parallel}(e_g)$  is proportional to  $n_{e_g}(t)S_z'(t)$ . This is in contrast with  $^{17}T_{2,2p_{\pi}}^{-1}(h_{\parallel})$  which expression,  $^{17}T_{2,2p_{\pi}}^{-1}(h_{\parallel}) \propto \int_0^\infty d\tau \langle S_z'(\tau)S_z'(0) \rangle \cos(\omega\tau)$ , does not depend on  $n_{e_g}$ . The rate  $T_{2,e_g}^{-1}(h_{\parallel})$  is proportional to

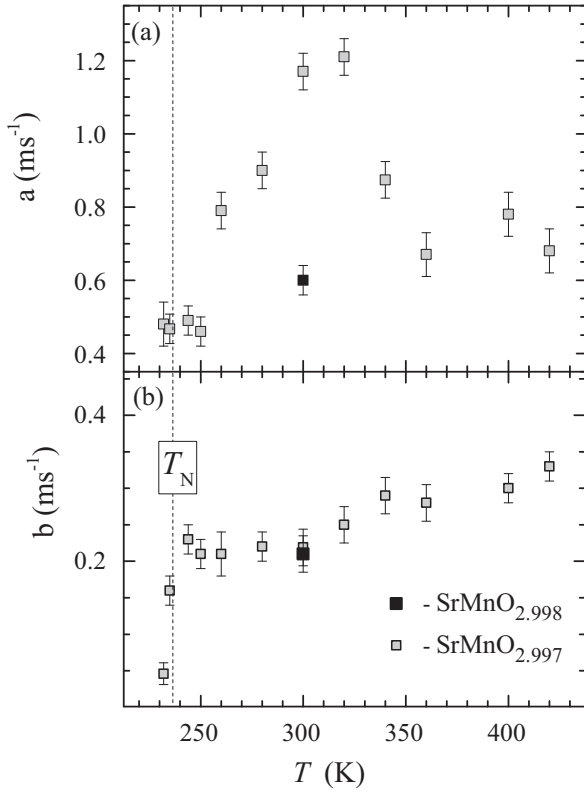


FIG. 8. Temperature dependence of (a) isotropic contribution  ${}^{17}T_{2,e_g}^{-1}(h_{\parallel}) \equiv a$  and (b) anisotropic contribution  ${}^{17}T_{2,2p_x}^{-1}(h_{\parallel}, \alpha) \equiv b(1 - 3 \cos^2 \alpha)^2$  to the rate  ${}^{17}T_2(h_{\parallel})^{-1}$ .

the spectral intensity built at  $\omega \ll \omega_{\text{NMR}}$  by the product of the correlation functions  $\langle n_{e_g}(t)n_{e_g}(0) \rangle$  and  $\langle S_z(t)S_z(0) \rangle$ . Indeed, the comparison of the two samples  $\text{SrMnO}_{2.997}$  and  $\text{SrMnO}_{2.998}$ , shows that on one hand  $T_{2,e_g}^{-1}(h_{\parallel})$  is sensitive to the electron doping level since it decreases in the less doped  $\text{SrMnO}_{2.998}$  and on the other hand,  ${}^{17}T_{2,2p_x}^{-1}(h_{\parallel})$  is not sensitive, as expected. The rate  $T_{2,e_g}^{-1}(h_{\parallel})$  shows an unusual behavior with a broad peak around 310 K in  $\text{SrMnO}_{2.997}$  [Fig. 8(a)]. It is worth to note that at high frequencies  $\omega = (1-4) \times 10^8 \text{ s}^{-1}$ , the thermal behavior of  $\langle n_{e_g}(t)n_{e_g}(0) \rangle$  shows no anomaly as deduced from  ${}^{17}T_1^{-1}(e_g)$  versus  $T$  data [Fig. 4(b)] in contrast to  $T_{2,e_g}^{-1}(h_{\parallel})$  which shows that at far lower frequencies  $\langle n_{e_g}(t)n_{e_g}(0) \rangle$  leads to an abnormal growth of the fluctuating  ${}^{17}h(e_g)$ .

In  $\text{SrMnO}_{2.997}$ , the nonmonotonic variation of  ${}^{17}T_{2,e_g}^{-1}(T)$  is caused by the slow-moving  $(2x - n_{e_g})$  electrons which create pulselike fluctuations of the local field at the  ${}^{17}\text{O}$  probe. Indeed, the slow diffusing motion of these electrons increases the efficiency of the DE mechanism, favoring FM correlated pairs of neighboring  $S(t_{2g})$  spins in the Mn- ${}^{17}\text{O}$ -Mn bond. This  ${}^{17}T_{2,e_g}^{-1}(T)$  unusual behavior indicates the presence of fluctuations of some short-range magnetic order (SRMO) at low-frequency in the range  $\omega_{\text{srmo}} = 2\pi {}^{17}T_{2,e_g}^{-1}(e_g)$ , i.e., fluctuations slower than  $10^3 \text{ s}^{-1}$ . The SRMO includes the change of spin configurations from AF to FM order of the two Mn neighbors in an Mn-O-Mn bond during the time  ${}^{17}T_{2,e_g}$ .

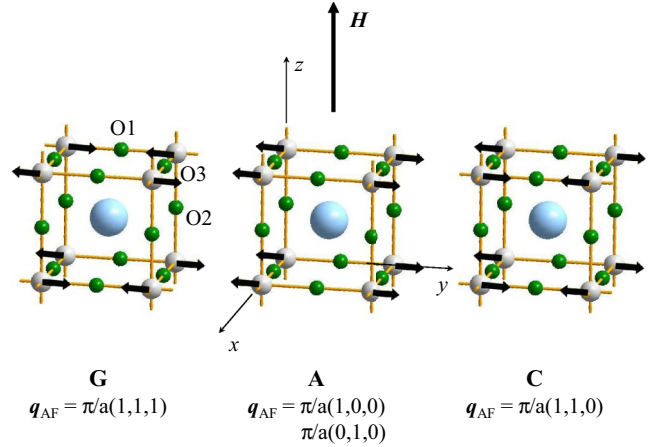


FIG. 9. AF spin configurations in the paramagnetic phase of cubic  $\text{SrMnO}_{2.997}$  in the magnetic field  $H = 117 \text{ kOe}$ .

In contrast to  ${}^{17}\text{O}$ , the  $T$  dependence of  ${}^{87}T_2^{-1}$  shows no anomaly (Fig. 5). Let us underline that each  ${}^{17}\text{Sr}$  probes the spin configurations of eight nearest Mn neighbors. The absence of anomaly means that the sum  $\sum_{i=1}^8 h_i(e_g)$  is zero, even if during the time  ${}^{87}T_2$  some pairs of  $S(t_{2g})$  neighbors become FM correlated within the cubic unit cell. Thus, with the  $T_{2,e_g}^{-1}$  results, we deduce from  ${}^{17}\text{O}$  that there is some short-range magnetic order at low-frequency whereas with  ${}^{17}\text{Sr}$ , we deduce that FM order should be excluded within the *cubic unit cell*. So that the scrolling of different  $S(t_{2g})$  environments experienced by both NMR probes O and Sr leads only to the following AF orders in the *cubic unit cell* (Fig. 9): AF-G [ $q = \pi/a(1, 1, 1)$ ], AF-C [ $q = \pi/a(1, 1, 0)$ ], and AF-A [ $q = \pi/a(0, 0, 1)$ ] [3]. Thus in cubic  $\text{SrMnO}_{3-x}$  the slow fluctuating short-range magnetic order is built from these three AF ordered unit cells. Being short range, the SRMO involves slow fluctuation of spin correlations of Mn neighbors in nanodomains built with a restricted number of unit cells; its proposed description is as follows. Pairs of neighboring AF coupled  $S(t_{2g})$  spins fluctuate rapidly ( $\uparrow\downarrow \leftrightarrow \downarrow\uparrow$ ) with the time constant  $\tau_c = 2\pi/\omega_{\text{ex}}$ , while the AF configurations of the eight  $S(t_{2g})$  spins within the cubic unit cell is stable during a much longer time,  $\tau_{c,\text{srmo}} = 2\pi/\omega_{\text{srmo}}$  corresponding to fluctuations slower than  $10^3 \text{ s}^{-1}$ . During this long time, the staggered moments of the spin configuration rotate perpendicularly to  $H$  minimizing the magnetic energy of these nanodomains, as  $H > H_{\text{spin-flop}}$ .<sup>3</sup>

The existence in the PM state of C and A-type AF configured cubic cells which are of reduced dimensionality (Fig. 9) most likely explains the gaplike thermal behavior of the magnetic susceptibility.

<sup>3</sup>In the low-temperature phase, the value of  $H_{\text{spin-flop}}$  is estimated as 20 kOe, with the expression  $H_{\text{spin-flop}} = (H_a H_{\text{ex}})^{0.5}$  using the magnetic field anisotropy  $H_a = 200 \text{ Oe}$  and the exchange field  $H_{\text{ex}} = 1 \times 10^6 \text{ Oe}$ . In the PM phase this  $H_{\text{spin-flop}}$  estimation is an upper limit.

#### IV. CONCLUSIONS

The manganese oxide SrMnO<sub>3</sub> with the  $Pm\bar{3}m$  crystal structure is a rare example of cubic antiferromagnet. A lightly electron-doped SrMnO<sub>2.997</sub> polycrystalline sample has been studied in the PM phase with <sup>17</sup>O and <sup>17</sup>Sr NMR measurements.

The gaplike peculiar behavior of the bulk magnetic susceptibility  $d\chi/dT \geq 0$ , is due to the spin susceptibility  $\chi_s$  of the localized spins  $S(t_{2g})$  of the Mn ions, as deduced from <sup>17</sup>O and <sup>17</sup>Sr NMR shift data. Such  $T$  dependence of  $\chi$  being typical of compounds with low dimensional AF configuration suggests that in the PM phase some short-range magnetic orders of the  $S(t_{2g})$  spins with a lower-dimensional AF configuration should add to the main three dimensional AF-G type configuration. We have focused our study on the low-energy spin excitations in the PM phase by measuring the spin-lattice  $T_1^{-1}$  and the spin-echo decay  $T_2^{-1}$  rates of both probe nuclei in the PM phase. Thus the time-dependent part of the hyperfine fields  $^{17}h(e_g)$ ,  $^{87}h(e_g)$ , and  $^{17}h(2p_\pi)$  at low frequencies were investigated.

The thermal behavior of  $^{17}T_1^{-1}(2p_\pi) \propto T$  indicates an almost  $T$ -independent value of the characteristic energy of the damped magnon excitations of the AF coupled  $S(t_{2g})$  Mn spins,  $\hbar\omega_{sf}$ , at  $q \ll \pi/a$ . Moreover the deduced  $T$ -independent behavior of  $\chi_s(q)/\omega_{sf}(q)$  ratio at  $q \ll \pi/a$ , indicates a high thermal stability of the fluctuating short-range magnetic order in the PM phase of SrMnO<sub>2.997</sub>.

The echo-decay rate  $^{17}T_2^{-1}$  probes the fluctuations of the neighboring  $S(t_{2g})$  spins at  $\omega \ll \omega_{nmr}$ . The contribution  $^{17}T_{2,e_g}^{-1}$  is proportional to the spectral intensity of the correlation function,  $\langle n_{e_g}(t)n_{e_g}(0) \rangle$ , where  $n_{e_g}$  is the number of fast-moving doped electrons per Mn with  $n_{e_g} \leq 2x$ . Consistently, our results show that  $^{17}T_{2,e_g}^{-1}$  is sensitive to the electron doping level since it decreases from SrMnO<sub>2.997</sub> to the less doped sample SrMnO<sub>2.998</sub>. As shown by our shifts data,  $n_{e_g}$  decreases down to  $T_N$ , so that a fraction  $(2x - n_{e_g})$  of the doped  $e_g$  electrons

slow down their Mn-Mn hopping providing local changes of the double-exchange interaction which favor FM correlated pairs of neighboring  $S(t_{2g})$  spins in the Mn – <sup>17</sup>O – Mn bond. The rate  $^{17}T_{2,e_g}^{-1}$  exhibits an unusual behavior with a broad peak around 310 K in SrMnO<sub>2.997</sub>. This nonmonotonic variation which is caused by the slow-moving  $(2x - n_{e_g})$  doped electrons indicates low-frequency ( $\omega_{srmo} \leq 10^3 \text{ s}^{-1}$ ) fluctuations of the short-range magnetic order which may include the change of AF  $\leftrightarrow$  FM spin alignment of neighboring magnetic ions.

For the <sup>17</sup>Sr nuclei, which probe the spin configuration of eight neighboring Mn in the cubic unit cell, there is no  $T_2^{-1}$  anomaly. With the  $^{87}T_{2,e_g}^{-1}$  results, we deduce that FM order should be excluded within *the cubic unit cell*. Both NMR probes lead only to the following AF orders in the *cubic unit cells*: AF-G [ $\mathbf{q} = \pi/a(1, 1, 1)$ ], AF-G [ $\mathbf{q} = \pi/a(1, 1, 0)$ ], and AF-A [ $\mathbf{q} = \pi/a(0, 0, 1)$ ] so that the slow fluctuating short-range magnetic order is built from these three AF ordered unit cells shown in Fig. 9.

Finally, in contrast to the AF state where FM ordered nanoregions like small-size magnetic polarons are created by the doped electrons below 50 K, our study reveals that no FM ordered cubic unit cells may appear in the PM state so that more complicated AF short-range spin order exists above  $T_N$  in cubic SrMnO<sub>3-x</sub>.

#### ACKNOWLEDGMENTS

The research was carried out within the state assignment of Ministry of Science and Higher Education of the Russian Federation (theme “Function” No. AAAA-A19-119012990095-0) and supported in part by the Russian Foundation of Basic Researches (project No. 18-32-00030). A.G. and S.V. are grateful to ESPCI for hospitality and support.

- 
- [1] T. Negas and R. Roth, *J. Solid State Chem.* **1**, 409 (1970).  
 [2] O. Chmaissem, B. Dabrowski, S. Kolesnik, J. Mais, D. E. Brown, R. Kruk, P. Prior, B. Pyles, and J. D. Jorgensen, *Phys. Rev. B* **64**, 134412 (2001).  
 [3] E. Wollan and W. Koehler, *Phys. Rev.* **100**, 545 (1955).  
 [4] A. Trokiner, S. Verkhovskii, Z. Volkova, A. Gerashenko, K. Mikhalev, A. Germov, A. Yakubovskii, A. Korolev, B. Dabrowski, and A. Tyutyunnik, *Phys. Rev. B* **93**, 174413 (2016).  
 [5] D. Teaney, M. Freiser, and R. Stevenson, *Phys. Rev. Lett.* **9**, 212 (1962).  
 [6] L. de Jongh and A. Miedema, *Adv. Phys.* **50**, 947 (2001).  
 [7] R. Coldea, R. A. Cowley, T. G. Perring, D. F. McMorrow, and B. Roessli, *Phys. Rev. B* **57**, 5281 (1998).  
 [8] A. A. Belik, Y. Matsushita, Y. Katsuya, M. Tanaka, T. Kolodiaznyi, M. Isobe, and E. Takayama-Muromachi, *Phys. Rev. B* **84**, 094438 (2011).  
 [9] H. Sakai, S. Ishiwata, D. Okuyama, A. Nakao, H. Nakao, Y. Murakami, Y. Taguchi, and Y. Tokura, *Phys. Rev. B* **82**, 180409(R) (2010).  
 [10] C. Chiorescu, J. L. Cohn, and J. J. Neumeier, *Phys. Rev. B* **76**, 020404(R) (2007).  
 [11] H. Meskine, H. König, and S. Satpathy, *Phys. Rev. B* **64**, 094433 (2001).  
 [12] J. van den Brink and D. Khomskii, *Phys. Rev. Lett.* **82**, 1016 (1999).  
 [13] A. M. Oleś and G. Khaliulin, *Phys. Rev. B* **84**, 214414 (2011).  
 [14] J.-S. Zhou and J. B. Goodenough, *Phys. Rev. B* **68**, 054403 (2003).  
 [15] P.-G. de Gennes, *Phys. Rev.* **118**, 141 (1960).  
 [16] A. Germov, A. Trokiner, Z. Volkova, K. Mikhalev, A. Gerashenko, S. Verkhovskii, A. Korolev, I. Leonidov, E. Konstantinova, and V. Kozhevnikov, *Phys. Rev. B* **96**, 104409 (2017).  
 [17] A. Narath, *Hyperfine Interactions* (Academic Press, New York, 1967).  
 [18] L. Vaugier, H. Jiang, and S. Biermann, *Phys. Rev. B* **86**, 165105 (2012).  
 [19] C. Zener, *Phys. Rev.* **82**, 403 (1951).



- [20] E. Andrew and D. Tunstall, *Proc. R. Soc. London* **78**, 1 (1961).
- [21] D. Freude and J. Haase, *Quadrupole eEffects in Solid-State Nuclear Magnetic Resonance* (Springer-Verlag, Berlin Heidelberg, 1993).
- [22] C. Pennington, V. Stenger, C. Recchia, C. Hahn, K. Gorny, V. Nandor, D. Buffinger, S. Lee, and R. Ziebarth, *Rhys. Rev. B* **53**, R2967 (1996).
- [23] C. Slichter, *Principles of Magnetic Resonance* (Springer-Verlag, Berlin, 1990), p. 640.
- [24] R. Nathans, F. Menzinger, and S. Pickart, *J. Appl. Phys.* **39**, 1237 (1968).
- [25] A. Narath, *Phys. Rev. B* **13**, 3724 (1976).
- [26] R. Walstedt and S.-W. Cheong, *Rhys. Rev. B* **51**, 3163 (1995).
- [27] A. Trokiner, S. Verkhovskii, A. Yakubovskii, A. Gerashenko, P. Monod, K. Kumagai, K. Mikhalev, A. Buzlukov, Z. Litvinova, O. Gorbenko, A. Kaul, and M. Kartavtzeva, *Phys. Rev. B* **79**, 214414 (2009).
- [28] T. Kohmoto, T. Goto, S. Maegawa, N. Fujiwara, Y. Fukuda, M. Kunitomo, and M. Mekata, *Phys. Rev. B* **49**, 6028 (1994).
- [29] S. Baek, F. Borsa, Y. Furukawa, Y. Hatanaka, S. Kawakami, K. Kumagai, B. Suh, and A. Cornia, *Phys. Rev. B* **71**, 214436 (2005).