**NMR and spin relaxation in LaGa$_{1-x}$Mn$_x$O$_3$: Evidence for thermally activated internal dynamics**

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Single crystals of diamagnetically diluted manganites, LaGa$_{1-x}$Mn$_x$O$_3$ ($x = 0–0.2$) have been investigated by means of magnetic-resonance techniques. Detailed study was performed of the NMR line shape, spin-spin and spin-lattice nuclear relaxation of $^{69}$Ga and $^{71}$Ga nuclei. The analysis of the temperature and concentration dependencies of the spin-relaxation rates was supported by additional measurements on $^{139}$La nuclei and electron-spin resonance on Mn electron-spin system. The electrical quadrupole mechanism of nuclear-spin relaxation is shown to be dominant at low Mn concentration ($x \leqslant 0.005$), whereas the magnetic dipolar interaction with the Mn electron spins is prevalent at $x \geqslant 0.02$. The obtained data suggest the presence of thermally activated internal motion with the activation energy of about 50 meV that governs the Mn$^{3+}$ electron spin-lattice relaxation and, via dipolar interaction, the nuclear-spin relaxation of the host nuclei. In the scenario suggested, this motion can be related to the hindered Jahn-Teller dynamics of the Mn$^{3+}$ ions linked to clusters or pinning defects.

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**I. INTRODUCTION**

In recent years rare-earth perovkite-type manganites have attracted much attention due to their unusual magnetic and transport properties, including the colossal magnetoresistance (CMR) effect observed in manganites doped with alkali-earth divalent ions (see, for example, the review articles 1–3 and references therein). Despite enormous efforts undertaken in recent years, it is not yet possible to obtain full understanding of the nature of effects observed in these materials.

The parent compound LaMnO$_3$ is an antiferromagnetic insulator below $T_N = 140$ K; at room temperature, it has orthorhombic crystal structure and shows orbital ordering (OO), which consists of alternative staggered arrangements of $d_{3z^2 - r^2}$ and $d_{3x^2 - r^2}$ orbitals of the Mn$^{3+}$ ions. The OO is associated with cooperative deformation of the MnO$_6$ octahedra distorted by static Jahn-Teller (JT) effect so that their long axes alternate in the basal plane. The transition from the static to cooperative dynamic JT effect occurs at $T_{JT} = 750$ K accompanied by structural phase transition from the distorted orthorhombic ($O'$) to the cubic ($O$) phases (see, for example, Refs. 4 and 5).

Doping of the parent compound with divalent ions (Ca, Sr, etc.) leads to the partial oxidation of Mn ions from Mn$^{3+}$ to Mn$^{4+}$ and drastic changes in magnetic and transport properties of the material. Depending on doping concentration, mixed-valence manganites demonstrate a number of interesting effects, including the metal-type conductivity, ferromagnetic ordering, and colossal magnetoresistance effect, which are commonly explained through double exchange mediated by the hole hopping between Mn$^{3+}$ and Mn$^{4+}$ ions. 1–3

It appears, however, that the partial substitution of Mn$^{3+}$ ions with nonmagnetic ones (Ga$^{3+}$, Sc$^{3+}$) also leads to ferromagnetism and gradual decrease of the lattice distortion $^{6–9}$ the effects in some way similar to those observed in mixed-valence manganites, but obviously not related to the double exchange mechanism. Note, that in weakly doped LaMn$_{1 - x}$Sr$_x$O$_3$, where the role of the double exchange is very low, the temperature of the dynamic JT effect is drastically reduced in comparison with an undoped compound. $^5,10$

Apparently, doping with nonmagnetic non-JT ions leads to a partial removal of the strict ordering of JT distortions and appearance of dynamic reorientations. Interplay between correlated JT reorientations and ferromagnetic-type exchange is discussed by Goodenough et al. $^{6,7}$ One can expect that at increasing degree of dilution by nonmagnetic ions, the JT dynamics of Mn$^{3+}$ becomes more and more unbound, reaching pure dynamic JT effect for noninteracting isolated Mn$^{3+}$ ions in the diamagnetic host.

Evolution of spin and JT dynamics of manganese ions can be studied by magnetic-resonance methods in the systems of LaGa$_{1-x}$Mn$_x$O$_3$, where paramagnetic JT Mn$^{3+}$ ions are partially substituted by nonmagnetic non-JT Ga$^{3+}$ ions. NMR and spin-relaxation studies on $^{71}$Ga, $^{69}$Ga, and $^{139}$La nuclei provide direct information on internal fields and their dynamics in well-defined sites in the crystal lattice. In their turn, electron-spin resonance (ESR) spectra are sensitive to the JT effect and exchange interaction between magnetic ions. Note, that electric and magnetic properties of mixed LaMn$_3$O$_7$–LaGaO$_3$ compounds (mostly at high Mn concentration) have been studied recently $^{6–9,11–13}$ however, magnetic-resonance methods have not been used.

In the present paper, we report the detailed studies of $^{71}$Ga and $^{69}$Ga NMR and spin-relaxation dynamics in the series of single crystals of LaGa$_{1-x}$Mn$_x$O$_3$ in the temperature range of 190–380 K complemented by data on $^{139}$La spin relaxation and analysis of the ESR spectra. Much attention is paid to the systems with low manganese concentration ($x \leqslant 0.2$). The results are interpreted in the frames of JT configuration reorientations of the Mn$^{3+}$ ions which are incor-
porated into ferromagnetically coupled clusters or situated close to pinning defects. It is shown that the reorientation rate increases under heating with the Arrhenius law. The activation energy and rate constants of the JT dynamics are estimated.

II. EXPERIMENT

Crystals of LaGa$_{1-x}$Mn$_x$O$_3$ with $0 \leq x \leq 0.2$ were grown by the Czochralski technique in a slightly oxidizing atmosphere. According to the x-ray diffraction analysis, the lattice parameters depend on the composition in the way quite similar to the results reported previously. LaMnO$_3$ has a distorted orthorhombic $Pbnm$ crystal lattice of $O'$ type ($c/\sqrt{2} < a,b$). With a decrease in Mn concentration, the lattice changes from the $O'$ type at 100% of Mn to $O^\#$ type ($a,b \sim c/\sqrt{2}$) at 50% Mn or less. According to Ref. 7, this implies that there is no more preferable orientation of occupied $e_g$ orbitals of Mn$^{3+}$ ions in the crystals with 50% or less of Mn concentration.

Main NMR measurements were performed on Ga nuclei ($^{69}$Ga and $^{71}$Ga) in crystals with concentrations of 0%, 0.5%, 2%, 5%, 10%, 20% of Mn ions in the temperature range of 190–380 K. Some measurements were made on $^{139}$La nuclei. Bruker NMR spectrometer operating at 300 MHz proton frequency (7 T magnetic field) was used in the experiments. The resonant frequencies $v_0$ for $^{69}$Ga, $^{71}$Ga, and $^{139}$La were of 72 MHz, 91.5 MHz, and 42.1 MHz, respectively. The duration of the $\pi/2$ pulse was 1.5 $\mu$s that allowed us to excite and observe the quadrupolar spectrum of Ga nuclei. The spin-lattice relaxation time ($T_1$) was measured by the saturation-recovery method, the spin-spin-relaxation time ($T_2$) was studied by the spin-echo decay. The ESR spectra were measured in the same materials in IRE RAS, Moscow, using Bruker ER-200 Spectrometer (X band, 9.8 GHz) with the Oxford variable temperature system in the temperature range of 4–300 K.

III. RESULTS AND DISCUSSION

A. NMR spectra

Gallium isotopes, $^{69}$Ga and $^{71}$Ga, have a spin $I=3/2$ and gyromagnetic ratios of $^{69}\gamma=6.4 \times 10^7$ T$^{-1}$ s$^{-1}$ and $^{71}\gamma=8.15 \times 10^7$ T$^{-1}$ s$^{-1}$, nuclear quadrupole moments of $^{69}Q=0.168 \times 10^{-28}$ m$^2$ and $^{71}Q=0.106 \times 10^{-28}$ m$^2$ (in the electron charge units), and natural abundances of $^{69}P=60\%$ and $^{71}P=40\%$ for $^{69}$Ga and $^{71}$Ga, respectively.

At low Mn concentrations ($x=0$ and 0.005), the $^{71}$Ga and $^{69}$Ga NMR spectra demonstrate distinct quadrupole splitting. According to the symmetry of the perovskite crystal, there are, in general, four magnetically inequivalent Ga (or Mn) sites in the unit cell, and thus four different NMR spectra for an arbitrary orientation of the magnetic field $B_0$, each containing a central line (transition 1/2, $−1/2$) and two satellites: (3/2, 1/2) and (−1/2, −3/2). If $B_0$ lies in one of the principal crystalline planes, only two quadrupolar triplets are observed, and they are merged into one when $B_0$ lies along the $a$, $b$, or $c$ axis. From the rotation patterns for $^{71}$Ga (see Fig. 1), we estimated the quadrupole coupling constant and asymmetry parameter as $\nu_Q=1.28$ MHz and $\eta=0.27$, respectively. The $\nu_Q$ value was compared with that calculated from the positions of the oxygen atoms using point-charge approximation; a good agreement is attained with a fair assumption for the antishielding factor to be in the order of 0.4.

With increase of the Mn concentration up to $x=0.02$, the satellites become broader, and cannot be distinguished at $x>0.05$. Apparently, this broadening is related to the strong local crystal-field distortions induced by the substitution of Ga$^{3+}$ with Mn$^{3+}$ ions. The quadrupole-related broadening of the central line is of the second order in $\nu_Q/v_0$ and not so pronounced.

B. The shift and shape of the NMR line

The evolution of the central NMR line with an increase of Mn concentration is shown in Fig. 2. In Fig. 3, the central line is shown at different temperatures for the sample with $x=0.1$. The linewidth increases with increase in the Mn concentration as well as with decrease in temperature. At low concentrations ($x<0.02$), the line is broader for the $^{69}$Ga than $^{71}$Ga, indicating predomination of the quadrupolar mechanism of the broadening ($^{69}Q^{>^{71}Q}$), while in the samples with higher concentration, the situation is the opposite with the line broader for the $^{71}$Ga isotope, pointing to the dominant role of the magnetic mechanism ($^{71}\gamma^{>^{69}\gamma}$).

As one can see in Figs. 2 and 3, at higher $x$, the shape of the line becomes asymmetric with an additional broad component which is shifted to higher frequencies with decreasing temperature. The shape of the line can be described with a sum of Gaussian (central) and Lorentzian (shifted) components as

$$g(\nu) = A_G \exp \left( -\frac{(\nu - \nu_G)^2}{2 \delta^2_G} \right) + \frac{A_L}{1 + \frac{(\nu - \nu_L)^2}{\delta^2_L}},$$

where $A_G$, $\nu_G$, and $\delta_G$ are the areas, central frequencies, and linewidths of the Gaussian components, and $A_L$, $\nu_L$, and $\delta_L$ are the areas, central frequencies, and linewidths of the Lorentzian components.
with the first spectral moment as 15

gin. The effect of the paramagnetic centers can be described

proportional to the temperature, indicating their paramagnetic ori-

d of the Gaussian and Lorentzian components, respectively.

central frequencies, and

A G

\delta G, \delta L

where

\text{normalized to the same height. Solid curves are the best fits by Eq. (1); dotted curves show the Gaussian and Lorentzian components for } x = 0.05. Inset: the Gaussian width vs } x \text{ for } \text{A Ga (filled symbols) and } \text{A Ga (open symbols).}

\text{The shifts of the both } \nu G \text{ and } \nu L \text{ are inversely propor-

tional to the temperature, indicating their paramagnetic or-

gen. The effect of the paramagnetic centers can be described with the first spectral moment as 15

M 1 = 2SPS(aIS)

(2)

\text{where } A G, A L \text{ are the relative amplitudes, } \nu G, \nu L \text{ are the}

G

\delta G, \delta L \text{ are the characteristic widths of the Gaussian and Lorentzian components, respectively.}

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tional to the temperature, indicating their paramagnetic or-

\text{assuming the ESR frequency of } \nu e = 2 \times 10^{11} \text{ Hz at } 7 \text{ T,}

\text{we estimated } p_s \text{ with the Brillouin function (for } T = 300 \text{ K, it}

\text{yields } p_s \sim 0.03, \text{ and calculated the shift of the NMR line}

\text{induced by the demagnetization field. It appears that the shift}

\text{of the Gaussian component is in a very good quantitative}

\text{agreement with our calculations, including dependences on}

\text{the temperature, concentration of Mn, and shape of the}

\text{sample. This shift is relatively moderate (about 200 ppm at}

\text{300 K) and will be not discussed further in the paper.}

\text{The shift of the Lorentzian component is much higher.}

\text{The temperature dependence of the contribution additional to}

\text{the demagnetization field } \nu L - \nu G \text{ is shown in the inset in}

\text{Fig. 3. As one can see, the shift is also inversely proportional}

\text{to the temperature and grows with increase in the concentra-

\text{tion of Mn. Apparently, it is related to the first (“internal”)}

\text{term in Eq. (3), which might not be equal to zero due to the}

\text{isotropic hyperfine interactions with Mn^{3+} ions located close}

\text{of those particular nuclei. For comparison, the hyperfine}

\text{interaction of } ^{139}\text{La with the nearest neighboring Mn^{3+} (they}

\text{are located at the distance of } 3.8 \text{ Å, see Ref. 9) is in the}

\text{order of } 0.5 \text{ T (Ref. 16), leading to the shift of about } 10^3 \text{ppm}

\text{(at } p_s = 0.03, \text{ about three times higher than that observed).}

\text{The concentration dependence of the line width is shown in}

\text{Fig. 2 (inset). At } x \approx 0.05, \text{ both } \delta G \text{ and } \delta L \text{ (not shown in}

\text{the figure) grow with increase in the concentration of Mn.}

\text{Besides, they are inversely proportional to the temperature.}

\text{The relative values of the width (normalized to the NMR}

\text{frequency) are the same for the both isotopes of Ga. All of}

\text{this indicates the magnetic mechanism of the NMR broaden-

\text{ing due to the interaction with Mn ions. Taking into account}

\text{that the electron relaxation rate is much higher than the}

\text{nuclear dephasing rate (} T_2^* \text{)}, \text{one can expect partial aver-

\text{aging of the electron local fields as 16}

\text{M 2}^{IS} = p_s^2(M 2^{IS}_0)

(4)

\text{where } M 2^{IS} \text{ is the second moment of the NMR spectral line,}

\text{and } (M 2^{IS}_0) \text{ is the static second moment (in the absence of}

\text{the electron flips). For } x = 0.1 \text{ and } 300 \text{ K, according to our}

\text{estimations, } (M 2^{IS})_0^{1/2}/\nu_0 \sim 180 \text{ ppm, which is in a good}

\text{agreement with the experimental } \delta L \text{ (Fig. 2, inset). Note that}

\text{the broadening due to the Ga-Ga dipolar interactions can be}

\text{estimated as of } 1 \text{ kHz } (\sim 10 \text{ ppm}), \text{ that is much less than the}

\text{linewidth observed in our materials.}
the central transition proportional to a good correlation with the experimental finding, I_i corresponding rate of the echo decay is proportional to the second, due to the strong inhomogeneous broadening.

significant, first, due to the presence of both isotopes and, intermediate between Gaussian and Lorentzian the Mn concentration increases, the decay kinetics remaining.

It implies that in this range of Mn concentration, echo decay is determined by dipole-dipole interactions of Ga nuclei. According to our estimations, the major role is played by “instantaneous spectral diffusion” caused by the change in the sign of the dipolar field due to the π pulse.\(^{17,18}\) The corresponding rate of the echo decay is proportional to the \(\tilde{H}_i^2\tilde{H}_j^2\) term of dipolar interaction. It yields the \(T_2^{-1}\) value on the central transition proportional to \(\alpha P \alpha \gamma^2 (\alpha = 69, 71)\), in good correlation with the experimental finding. \(^{69}\)\(T_2\)/\(^{71}\)\(T_2\) = 1.3. The effect of flip-flops (the \(\tilde{H}_i^2\tilde{H}_j^2\) terms) is less significant, first, due to the presence of both isotopes and, second, due to the strong inhomogeneous broadening.

At the samples with \(x \geq 0.05\), the \(T_2\) value decreases as the Mn concentration increases, the decay kinetics remaining intermediate between Gaussian and Lorentzian (Fig. 4). The orientation dependence gradually weakens and disappears with the increase of \(x\). Decay time constants become temperature dependent, the \(^{69}\)\(T_2\)/\(^{71}\)\(T_2\) ratio being more than unity. All these facts suggest that the relaxation mechanism is governed by dipolar magnetic interactions between the Ga nuclear and \(\text{Mn}^{3+}\) electron spins. In Table I, the echo-decay times (in Gaussian approximation) are given for both Ga isotopes at \(x = 0.1\).

Taking into account that the nuclear spin \(I = 3/2\), and the echo is observed at the central transition, the contribution from the fluctuating fields induced by paramagnetic electrons can be described as

\[
(T_2^{IS})^{-1} = (\gamma_n H_L)^2 \tau \left(0.8 + \frac{4.2}{1 + \omega_n^2 \tau^2}\right),
\]

where \(H_L^2\) is the averaged local-field amplitude squared, \(\tau\) is the correlation time, \(\omega_n\) is the NMR frequency, 0.8 and 4.2 are the coefficients defined by the matrix elements of the electron-nuclear dipole-dipole interaction.\(^{15}\) In the limiting so-called “slow motion” case

\[
\omega_n \tau \gg 1,
\]

the second (non-secular) term in the parentheses, Eq. (5), is negligible, while at fast motion limit,

\[
\omega_n \tau \ll 1,
\]

it is constant. Thus in both cases, the echo-decay rate is proportional to the correlation time \(\tau\). Comparing Eq. (5) with the experimental values from the Table I, we conclude that the \(^{69}\)\(T_2\)/\(^{71}\)\(T_2\) ratio is about 30% less than predicted by the \(\gamma^2\) scaling, and the correlation time of the process that governs the echo decay decreases with the increase of the temperature.

D. Nuclear spin-lattice relaxation

Before the close consideration of our experimental results let us first discuss some peculiarities in spin-lattice relaxation measurements of nuclei with spin \(I \geq 1/2\) and multilevel energy spectrum. As it is known,\(^{19}\) the recovery to equilibrium after the \(\pi/2\) pulse excitation applied at \(t = 0\) can be described as a sum of \(2I\) exponentials:

\[
S(t) = 1 - \frac{M(t)}{M_0} = \sum_{i=1}^{2I} A_i \exp(-r_i t),
\]

where \(M(t)\) and \(M_0\) are magnitudes of the magnetization at the time \(t\) and at equilibrium, respectively. The characteristic rates are \(r_i W_0\), where \(W_0\) is the minimal characteristic relaxation rate, and the \(r_i\) values are determined by the relaxation mechanism. Amplitudes \(A_i\) depend both on which transitions are saturated at \(t = 0\) as well as which spectral line is observed.

<table>
<thead>
<tr>
<th>(T(K))</th>
<th>200</th>
<th>295</th>
<th>368</th>
</tr>
</thead>
<tbody>
<tr>
<td>(^{69})(T_2) (ms)</td>
<td>0.65±0.1</td>
<td>0.8±0.1</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td>(^{71})(T_2) (ms)</td>
<td>0.5±0.1</td>
<td>0.6±0.1</td>
<td>0.75±0.1</td>
</tr>
</tbody>
</table>

FIG. 4. Kinetics of the nuclear spin echo: (a) for \(^{71}\)Ga at \(T = 297\) K and different Mn content, the \(x\) values are shown near the data; (b) for \(^{69}\)Ga (filled symbols) and \(^{71}\)Ga (open symbols) at \(x = 0.1\) and different temperatures indicated at the plot. The dotted curves are guides for the eyes.

C. Spin-echo decay \((T_2)\)

Spin echo is observed at all Mn concentrations. It indicates nonhomogeneous NMR broadening in all the samples, including undoped ones. At low concentrations \((x \leq 0.02)\), echo decay has kinetics intermediate between Gaussian and simple exponential, with the temperature-independent decay time \(T_2\) varying from 2 ms to 4 ms in the dependence on the relative orientation of the magnetic field \(B_0\) and crystal axes.

It implies that in this range of the Mn concentration, echo decay is determined by dipole-dipole interactions of Ga nuclei. According to our estimations, the major role is played by “instantaneous spectral diffusion” caused by the change in the sign of the dipolar field due to the \(\pi\) pulse.\(^{17,18}\) The corresponding rate of the echo decay is proportional to the \(\tilde{H}_i^2\tilde{H}_j^2\) term of dipolar interaction. It yields the \(T_2^{-1}\) value on the central transition proportional to \(\alpha P \alpha \gamma^2 (\alpha = 69, 71)\), in good correlation with the experimental finding. \(^{69}\)\(T_2\)/\(^{71}\)\(T_2\) = 1.3. The effect of flip-flops (the \(\tilde{H}_i^2\tilde{H}_j^2\) terms) is less significant, first, due to the presence of the both isotopes and, second, due to the strong inhomogeneous broadening.

At the samples with \(x \geq 0.05\), the \(T_2\) value decreases as the Mn concentration increases, the decay kinetics remaining intermediate between Gaussian and Lorentzian (Fig. 4). The orientation dependence gradually weakens and disappears with the increase of \(x\). Decay time constants become temperature dependent, the \(^{69}\)\(T_2\)/\(^{71}\)\(T_2\) ratio being more than unity. All these facts suggest that the relaxation mechanism is governed by dipolar magnetic interactions between the Ga nuclear and \(\text{Mn}^{3+}\) electron spins. In Table I, the echo-decay times (in Gaussian approximation) are given for both Ga isotopes at \(x = 0.1\).

Taking into account that the nuclear spin \(I = 3/2\), and the echo is observed at the central transition, the contribution from the fluctuating fields induced by paramagnetic electrons can be described as

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where \(H_L^2\) is the averaged local-field amplitude squared, \(\tau\) is the correlation time, \(\omega_n\) is the NMR frequency, 0.8 and 4.2 are the coefficients defined by the matrix elements of the electron-nuclear dipole-dipole interaction. In the limiting so-called “slow motion” case

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the second (non-secular) term in the parentheses, Eq. (5), is negligible, while at fast motion limit,

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\omega_n \tau \ll 1,
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it is constant. Thus in both cases, the echo-decay rate is proportional to the correlation time \(\tau\). Comparing Eq. (5) with the experimental values from the Table I, we conclude that the \(^{69}\)\(T_2\)/\(^{71}\)\(T_2\) ratio is about 30% less than predicted by the \(\gamma^2\) scaling, and the correlation time of the process that governs the echo decay decreases with the increase of the temperature.
In our case, the competition of the two mechanisms can occur: the quadrupolar mechanism with the relaxation due to the interaction of the nuclear quadrupole moment with fluctuations of the electrical-field gradient, and the magnetic mechanism due to the dipole-dipole or hyperfine interactions of the nuclei with paramagnetic centers.

At $I=3/2$, the solution of the system of the rate equations yields a sum of only two terms if the transition ($\pm 1/2$) is observed. Further, if only the central transition is saturated at $t=0$, and the quadrupolar mechanism of relaxation is effective (with the same transition probabilities for $\Delta m=\pm 1$ and $\pm 2$, where $m$ is magnetic quantum number), the relaxation kinetics should be a single exponential as

$$S(t) = \exp(-W_0 t). \quad (9)$$

In the other case, if the magnetic mechanism plays major role, the kinetics consists of two exponentials as

$$S(t) = 0.9 \exp(-6W_0 t) + 0.1 \exp(-W_0 t). \quad (10)$$

If the satellite lines are excited and measured, one should expect an acceleration of the relaxation rate comparing to that as measured at the central transition in the case of the quadrupolar mechanism, and its slowdown in the case of the magnetic mechanism. This fact can be used for identification of the nuclear relaxation mechanism, as it was done$^{20}$ for $^{139}$La in $La_{2/3}Ca_{1/3}MnO_3$.

In most of our experiments, both $\pi/2$ pulses (excitation and readout) corresponded to the central NMR transition while the excitation of the quadrupole satellites was low. According to Eqs. (9) and (10), the main part of the relaxation curve ($\approx 90\%$) can be described with one exponential, while the partial excitation of the satellites can increase the contribution of the second term.

Let us now report our experimental results, starting with the low concentration of Mn, $x \approx 0.005$. Typical relaxation kinetics are shown at Fig. 5(a). As one can see, the kinetics is a single exponential with the rate being higher for the isotope $^{69}$Ga than for $^{71}$Ga. Though the ratio $^{71}T_1 / ^{69}T_1 = 1.85$ is slightly less than $(^{69}Q/^{71}Q)^2 = 2.5$, there is no doubt of the domination of the quadrupolar mechanism at low $x$. That was also confirmed by the measurements of the relaxation of the satellite transitions, where the rate was faster than on the central line.

Dependence of $T_1$ on the temperature $T$ is shown in Fig. 5(b). $T_1$ is approximately proportional to $T^{-2.4}$, which is close to the relation of $T^{-2}$ typical of quadrupolar relaxation above the Debye temperature.$^{21}$

Let us now conclude with the case of low concentrations and discuss the major problem of our interest, the effect of the paramagnetic Mn ions. At $x \approx 0.02$, as it was mentioned above, the satellites are significantly broadened and practically not observable. Choosing the power of the first pulse low enough to minimize the effect of satellites, we observed the relaxation kinetics with the fast term prevailing, in agreement with the magnetic mechanism. Typical examples of the relaxation kinetics observed at various Mn concentrations and temperatures are shown at Fig. 6. As one can see in the figure, the relaxation kinetics of $^{69}$Ga and $^{71}$Ga isotopes are practically the same for the both isotopes (the experimental error is about $10\%$). The coincidence of the relaxation rates has been observed in all the samples at $x \approx 0.02$ and in the whole temperature range studied, indicating a negligible role of the quadrupolar mechanism of relaxation.

Consider the mechanism of the relaxation induced by magnetic dipole-dipole interactions between paramagnetic...
centers and nuclei. The relaxation rate of a nucleus $I_j$ sited at a distance $r_{ij}$ from a paramagnetic center $S_j$ reads

$$\left(T_i^{-1}\right)_0^{-1} = W_i = \left(\gamma_n H_i^{\perp}\right)^2 \frac{\tau}{1 + (\omega_n \tau)^2},$$

(11)

where $H_i^{\perp}$ is the amplitude of the fluctuating local field created by spin $S_j$. For dipole interactions $H_i^{\perp}$ is inversely proportional to $r_{ij}^3$; thus, the direct spin-lattice relaxation has different rates for the nuclei located at different distances from $S_j$. The kinetics of the nuclear-spin system observed in the experiment depends on the efficiency of the nuclear-spin diffusion (flip-flop processes). If the diffusion is efficient, the net kinetics is described by a sum of 21 exponentials, see Eq. (8). In the case of direct relaxation, the exponential terms in Eq. (8) must be substituted by the stretched exponentials of the form

$$S_i(t) = A_i \exp(-\sqrt{r_{ij}W_i})$$

(12)

with the $W_0 = (T_i^{-1})_0$ value found from Eq. (11) by substituting $\left(H_i^{\perp}\right)^2 = \langle H_i^{\perp}\rangle^2$ averaged over all nuclei and paramagnetic centers as

$$\langle H_i^{\perp}\rangle^2 = 0.4 \frac{16 \pi^3}{9} n^2 S(S + 1) \gamma^2 \hbar^2.$$  

(13)

Eqs. (11) and (13) describe the slowest term $W_0$ of the multilevel relaxation. To compare it with our experimental data, one should multiply the rate by $6$, see Eq. (10).

As seen from Fig. 6, the stretched-exponential kinetics well describes the experimental data for intermediate concentrations $x = 0.05–0.1$. At lower concentration $x = 0.02$, the relaxation curves approach exponential at the long-time scale while stretched-exponential kinetics is observed during the initial stage. In the most concentrated samples ($x = 0.2$), the kinetics again becomes simple exponential, see the inset in Fig. 6. Such a behavior is in good agreement with the theoretical model that predicts direct relaxation for nuclei sited inside a sphere with the characteristic “potential radius” $b$ from a paramagnetic center while nuclei outside the effective sphere relax through the spin diffusion. At low doping, only a small number of nuclei are located in such spheres. Their relative number increases with increase in the concentration of Mn, providing more and more contribution to the relaxation kinetics. At the high concentration, where almost all nuclei have a paramagnetic Mn center in close neighborhood, the relaxation is exponential again and governed by the rate corresponding to the shortest distance $r_{ij}^0$.

The evolution of the NMR line during the spin-lattice relaxation process is shown in Fig. 7. Fourier transform of the free-induction decay (FID) obtained in the experiment with the delay of 2 ms after the first $\pi/2$ pulse is compared with that obtained at the equilibrium. Asymmetry of NMR line is a bit weaker for the second case, however the relaxation rates for the central (Gaussian) part of the line and its high-frequency wing do not differ more than by 10–20%.

Temperature dependences of the relaxation rates are shown in Fig. 8. For each $x$, measurements were performed in a number of samples grown at the same conditions. The relaxation rates appear to be slightly different for different samples but with the same type of the temperature dependence. Figure 8 shows the data averaged for the samples with the same concentration.

The results can be summarized as following. (1) At $x = 0.02$, the temperature dependence of the rate is weak and nonmonotonous in the range of 190–380 K, with a maximum $T_i^{-1}$ at about 300 K. (2) At $x = 0.05, 0.1$, and $0.2$, the relaxation slows down steeply with increase in temperature.

![Figure 7](image1.png)  
**FIG. 7.** Evolution of the NMR shape during spin-lattice relaxation; the lower trace corresponds to 2 ms after the first pulse, upper one corresponds to equilibrium.

![Figure 8](image2.png)  
**FIG. 8.** Temperature dependencies of the Ga spin-lattice relaxation rate at Mn concentrations 0.02–0.2 (indicated at the plot). Solid curves are the fit with the parameters shown in the Table II. Inset: the relaxation rate vs $x$ at 300 K; the dotted curve is guide for the eyes.
This dependence can be described with the Arrhenius law
with the activation energy of about 550 K. (3) The relaxation rate depends on the concentration of Mn approximately as $x^2$
(see Fig. 8, inset) in the range of 0.02$\ll x\ll 0.1$, and weakens (saturates) at $x = 0.2$. (4) The time $T_1$ appears to be the same
for the both isotopes $^{69}$Ga and $^{71}$Ga.

The relaxation slowdown with the increase in the temperature is commonly associated with the thermally activated
acceleration of internal motion, i.e., decrease of the correlation time $\tau$ under the fast-motion condition, Eq. (7). Correspondingly, the maximum in $T_1^{-1}$ (see the data for $x = 0.02$) is to be associated with $\omega_c \tau = 1$. However, in the both cases Eqs. (11) predicts a relaxation rate dependent on the gyromagnetic ratio. In this case, at $\omega_c \tau \ll 1$, the $^{69}T_1 / ^{71}T_1$ ratio is expected to be $(^{71}/^{69}) \gamma^2 = 1.62$ while in the experiment $^{69}T_1 = ^{71}T_1$. Independence $T_1$ on $\gamma_n$ suggests that the slow motion regime, Eq. (6), is valid. In the slow motion limiting case Eq. (11) reads

$$ (T_1^{-1})_0 = \frac{\langle H_L^2 \rangle}{H_0^2} \tau^{-1}. $$

Thus, taking into account the data of Fig. 8, one has to admit that $\tau$ grows with the increase in temperature. This seems to be quite unusual and, in addition, not correlated with the temperature dependence of $T_2$, see Table I.

To get an additional information on $\tau$, we performed spin-lattice relaxation measurements on the central NMR transition of the $^{139}$La host nuclei ($I = 7/2$) in the material with $x = 0.05$. Similar to the Ga, the relaxation of La was found to be well described with a stretched exponential kinetics, Eq. (12), with the spin-lattice relaxation time, $^{139}T_1 = (4.2 \pm 0.4)$ ms at $T = 295$ K. Since only the central transition was excited and observed, the major contribution to the La relaxation comes from the term with $28W_0f$ (see Ref. 20), while the relaxation of Ga in these conditions is governed by the term with $6W_0$, see Eq. (10). Taking that into account, one can conclude that in a fast motion limit $^{139}T_1 / ^{71}T_1$ is expected to be $(6/28)(^{71}/^{139}) \gamma^2 \approx 1.0$, while at a slow motion $^{139}T_1 / ^{71}T_1 = 6/28 \approx 0.21$. The experiment yields $^{139}T_1 / ^{71}T_1 = 0.26 \pm 0.06$, confirming unambiguously the slow motion limit $\omega_c \tau \gg 1$.

E. Phenomenological model

Let us consider the assumption common for paramagnetic solids that the correlation time $\tau$ in Eq. (11) is determined by
electron spin flips with the characteristic electron spin-lattice
relaxation rate $T_1^{-1}$, Refs. 21–23. Assume that, in its turn,
the electron-spin relaxation is governed by some internal
motion with its own correlation time $\tau_e$ and can be described by the standard formula

$$ T_1^{-1} = \frac{R^2}{1 + (\omega_c \tau_e)^2}, $$

where $R$ is the amplitude of some fluctuating field that in-
duces the electron-spin relaxation, and $\omega_c$ is the ESR fre-

quency ($\sim 10^{12}$ s$^{-1}$ at 7 T). Substituting Eq. (15) for the correlation time $\tau$ into Eq. (14), and making use of Eqs. (10) and (13), one obtains

$$ T_1^{-1} = \frac{\langle H_L^2 \rangle}{H_0^2} \frac{R^2 \tau_e}{1 + (\omega_c \tau_e)^2}. $$

Thus, the maximum in the temperature dependence is reached now at

$$ \omega_c \tau_e = 1, $$

whereas slowing down of the relaxation rate with the temperature corresponds to

$$ \omega_c \tau_e \ll 1, $$

and is related to the increase of the rate of the thermally
activated process with

$$ \tau_e = \tau_0 \exp \left( \frac{E_a}{k_B T} \right), $$

where $(\tau_e)^{-1}$ is characteristic attempt frequency.

At first sight, the assumption of the increase of $T_1e$ with the temperature increasing contradicts to the results of the echo-decay measurements. It was argued in Sec. III C that, according to Eq. (5), $\tau$ decreases with heating resulting in the growth of $T_2$. However, that means only that spin-spin and
spin-lattice relaxation rates of Ga nuclei are determined by different processes. This assumption restricts the range of the acceptable $T_1e$ values. In fact, $T_1e$, substituted in Eq. (5) for $\tau$ must yield spin-spin-relaxation rates $T_2^{-1}$, which are no faster than the experimentally observed ones. Analysis demonstrates that the requirement is most strict for $x = 0.1$: in this case, $T_1e \approx 10^{-8}$ s. Taking into account the slow motion limit, Eq. (6), we can conclude that at $x = 0.1$ the $T_1e$ value is in the range

$$ 1.7 \times 10^{-9} \text{ s} < T_1e < 10^{-8} \text{ s}. $$

This condition will be used in fitting of the experimental data by Eqs. (15)–(19), as described below.

There are four fitting parameters that can be used for the fitting: $E_a$, $H_L$, $\tau_0$, and $R$. The activation energy is determined almost independently from the slope of the temperature dependences of Fig. 8. For all the samples, $E_a / k_B = (550 \pm 50)$ K. Then, using the nonmonotonous dependence $T_1^{-1}(T)$ observed at $x = 0.02$, we can find $\tau_0$ and the product $RH_L$ for this material. To move further, one has to make an additional assumption. Let us suppose, for instance, that the parameter $R$ is nearly the same for all the samples. Taking this suggestion and using the inequality (20), we have chosen the fitting parameters as shown in Table II. In the last column of Table II, $T_1e$ is calculated for 300 K. Fitting of the experimental data is demonstrated by the solid lines in Fig. 8.
F. Additional support: ESR data

ESR spectra of Mn in LaGa$_{1-x}$Mn$_x$O$_3$ single crystals have been studied in broad concentration and temperature ranges. Detailed results and analysis will be published elsewhere. Here we report some of the data to support the thermally activated motion model in LaGa$_{1-x}$Mn$_x$O$_3$ materials.

Figure 9 demonstrates the ESR spectra taken at different temperatures in the sample with $x=0.1$. The shape of the line can be fitted as a sum of two Lorenzian lines; the first one with the linewidth of 18 mT is temperature independent while the second one demonstrates steep broadening with decrease in temperature. Temperature dependence of the half-width of the latter component is shown in Fig. 10 together with the corresponding value of the inverse magnetic susceptibility $\chi^{-1}$, with the $x$ values found by double integration of the ESR absorption derivative. As one can see from Fig. 10, the experimental data can be fitted in the assumption of the thermally activated $\tau_e$ as described with Eq. (21),

$$
\gamma_e \Delta = \left[(R^2 \tau_e)^{-1} + (\gamma_e \Delta_x)^{-1}\right]^{-1} + \gamma_e \Delta_{inh},
$$

(21)

where $\Delta_{inh}$ is the temperature-independent contribution from inhomogeneous broadening, $R^2$ has nearly the same meaning as in Eq. (15), and $\Delta_x$ is the linewidth within static low-temperature limit (this term is added to avoid singularity at $\tau_e \rightarrow \infty$). As one can see from Fig. 10, the experimental data can be fitted in the assumption of the thermally activated $\tau_e$ as described with Eq. (21) and parameters $E_a = 550$ K; $\Delta_{inh} = 27$ mT, and $\Delta_x = 160$ mT. A significant number of fitting parameters as well as a relatively moderate range of the linewidth variation with temperature allow us to speak only qualitatively; nevertheless, these results confirm that thermally activated motion with the activation energy of about 500–600 K does exist in our material.

![Figure 9. ESR spectra of LaGa$_{0.9}$Mn$_{0.1}$O$_3$ at different temperatures (indicated on the plot).](image)

![Figure 10. Temperature dependence of the ESR line width at $x = 0.1$. Solid curve is calculated using Eq. (21). Inset: temperature dependence of the inverse ESR susceptibility; straight line shows the Curie-Weiss law.](image)

<table>
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<th>$x$</th>
<th>$E_a/k_B$ (K)</th>
<th>$H_L$ (Oe)</th>
<th>$\tau_{e0}$ ($10^{-14}$ s)</th>
<th>$R(10^{10}$ s$^{-1}$)</th>
<th>$T_{1e}$ at 300 K ($10^{-9}$ s)</th>
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TABLE II. Parameters used for fitting the spin-lattice relaxation data.
IV. FINAL DISCUSSION AND CONCLUSION

Let us now discuss a possible nature of the internal motion that determines the temperature dependence of the electron-spin relaxation and, as a sequence, the nuclear-spin-relaxation rate in our materials. One of the possible scenarios is related to thermally activated reorientations of JT configurations hindered in strongly coupled Mn\(^{3+}\) clusters or near pinning centers.

As it is known, in LaMnO\(_3\) there exists the static orbital ordering\(^1\)–\(^5\) the \(d_{3z^2-r^2}\) and \(d_{x^2-y^2}\) orbitals of neighboring Mn\(^{3+}\) ions, as well as corresponding elongated octahedra, are oriented perpendicular to each other till \(T_{JT} = 750\) K. In diluted materials, according to the model proposed by Goodenough et al.\(^6\), such an orientation remains to be preferable for some clusters where neighboring Mn\(^{3+}\) ions interact through isotropic ferromagnetic superexchange. Likely, in finite-size clusters, the orbital ordering is not so rigid as in the regular crystal lattice of LaMnO\(_3\), and one can expect thermally activated reorientations of mutually correlated orbitals. Similar hindered JT configuration reorientations can also occur with participation of defects that play role of pinning centers. According to our hypothesis, this is the internal motion that determines the correlation time \(\tau_c\) in Eq. (15) for electron spin-lattice relaxation.

In the frames of this consideration, it is clear that an increase in the Mn concentration leads to a gradual slowdown of JT reorientations, evolving from the case of pure dynamic JT effect at isolated Mn\(^{3+}\) centers in materials with small \(x\) to the thermally activated reorientations (quasistatic JT effect\(^6\)–\(^7\)) in materials with moderate concentrations of Mn (our samples with \(x = 0.02–0.2\)) and, finally, to the cooperative static orbital ordering at \(x\) approaching unity. In our case, the obtained activation energy of about 50 meV correspond to the lowest potential barrier for the JT configuration reorientations; typically, this value can be an order of magnitude lower than the total JT splitting (compare to similar \(E_a\) values found on the Cu\(^{2+}\) JT systems)\(^25\).

Let us return to the data in Table II. First, \(T_{1\ell}\) values are close to each other for all the materials. This fact implies the same origin of the paramagnetic centers which are responsible for nuclear relaxation. Comparing \(H_L\) from Table II to that in Eq. (13), the relative concentration of those centers can be estimated to about 10% of the nominal concentration of Mn, in agreement with estimations obtained from ESR (Sec. III F).

The evolution of the NMR line shape during the spin-lattice relaxation (Fig. 7) shows that the relaxation rate of the Lorentzian (shifted) and Gaussian (central) components of the NMR line do not differ considerably. At the same time, it is likely that the Lorentzian “wing” of the spectrum originates from the Ga nuclei situated close to the Mn\(^{3+}\) ions. Thus one can conclude that the majority of the Mn ions affect the shape and shift of the NMR line, but make negligible contribution to the spin-lattice relaxation rate. This provides an additional support to our assumption that only a minor part of the Mn ions (only those linked in clusters or pinning defects) participate in slow reorientations and so govern nuclear \(T_1\).

An origin of the echo decay in the samples under study is not clear enough. The experimental data indicate that \(T_2\) is determined by fluctuations which are still slower than those inducing spin-lattice relaxation. Apparently, there is a broad distribution of the clusters and pinning centers in our materials, and different centers can be the most efficient in spin-spin or spin-lattice relaxation.

Strict theoretical description of the ESR and spin-lattice relaxation in Mn clusters with the account made for thermally activated JT reorientations and superexchange is a complicated problem and beyond the frames of the present work. Nevertheless, some order-of-magnitude estimations can be performed. The parameter \(R\) in our model has meaning of the amplitude of fluctuations responsible for the electron spin-lattice relaxation of Mn ions. Thus it can be associated with a modulation of the rhombic (\(E\)) and axial (\(D\)) terms in the Mn\(^{3+}\) spin Hamiltonian, this modulation being induced by the orbital reorientations. According to Ref. 10, in LaMnO\(_3\) and related systems one has \(D/h \sim E/h \sim 10^{-10} – 10^{-11}\) s\(^{-1}\), in order with the data in Table II.

Another possible scenario can be related to hopping of a small polaron associated with a hole localized on the Mn\(^{4+}\) ion. The hopping of the hole between Mn\(^{4+}\) and Mn\(^{3+}\) ions can lead, through spin-orbital coupling, to the electron-spin relaxation. This mechanism was suggested by Shengelaya et al.\(^26\) for the concentrated CMR manganites doped with Ca. Slow thermally activated dynamics with the correlation times of the order of \(10^{-8} – 10^{-9}\) s was reported by Sakai et al.\(^20\) who studied the \(^{139}\)La spin-lattice relaxation in La\(_{2/3}\)Ca\(_{1/3}\)MnO\(_3\) and attributed this effect to spin-glass-like behavior of magnetic clusters. A maximum in the temperature dependence of the \(^{139}\)La nuclear spin-lattice relaxation rate in LaMnO\(_3\) was also observed by Allodi et al.\(^16\). The suggested mechanism was based on the isotropic hyperfine interaction modulated by thermally activated diffusion of a ferromagnetic excitation. In our samples, the Mn\(^{4+}\) ions are not specially introduced but can be present at low concentration due to slight nonstoichiometry in oxygen. However, the values of the activation energy for the polaron hopping as determined from the conductivity measurements on the same LaGa\(_{1-x}\)Mn\(_x\)O\(_3\) crystals\(^11\) fall within the range of 0.45–0.65 eV, an order of magnitude larger than \(E_a \sim 50\) meV. In addition, thermally activated polaron hopping would result not in narrowing but in broadening of the ESR line\(^26\) in opposite to what was experimentally observed.

In conclusion, in the current work we present the detailed study and analysis of NMR spectra, the NMR line shape, transverse and longitudinal nuclear relaxation of \(^{69}\)Ga and \(^{71}\)Ga in the LaGa\(_{1-x}\)Mn\(_x\)O\(_3\) single crystals at \(x = 0–0.2\). The analysis of the temperature dependencies of the spin-relaxation rates supported by additional measurements on \(^{139}\)La and ESR studies demonstrates the presence of thermally activated motion that can be related to the hindered reorientations of JT orbital configuration of Mn\(^{3+}\) ions linked to the clusters or pinning defects. The activation energy is about 50 meV. We believe this corresponds to the intermediate (quasistatic) JT regime that takes place in diluted manganites with finite-size clusters. Further investigation, both theoretical and experimental (in an extended tem-
perature range) would be appropriate to test and develop the proposed model.

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