Charge and Orbital Ordering in Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ Studied by $^{17}$O NMR

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The charge and orbital ordering in Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ is studied for the first time by $^{17}$O NMR. This local probe is sensitive to spin, charge and orbital correlations. Two transitions exist in this system: the charge and orbital ordering at $T_{CO} = 225K$ and the antiferromagnetic (AF) transition at $T_N = 170k$. Both are clearly seen in the NMR spectra measured in a magnetic field of $7T$. Above $T_{CO}$ there exists only one NMR line with a large isotropic shift, whose temperature dependence is in accordance with the presence of ferromagnetic (FM) correlations. This line splits into two parts below $T_{CO}$, which are attributed to different types of oxygen in the charge/orbital ordered state. The interplay of FM and AF spin correlations of Mn ions in the charge ordered state of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ is considered in terms of the hole hopping motion that is slowed down with decreasing temperature. The developing fine structure of the spectra evidences, that there still exist charge-disordered regions at $T_{CO} > T > T_N$ and that the static ($t < 10^{-6}s$) orbital order is established only on approaching $T_N$. The CE-type magnetic correlations develop gradually below $T_{CO}$, so that at first the AF correlations between checkerboard ab-layers appear, and only at lower temperature - CE correlations within the ab-planes.

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I. INTRODUCTION

The charge ordering phenomena in the hole-doped R$_{1-x}$A$_x$MnO$_3$ (R is a rare-earth ion and A is a divalent alkaline-earth ion) have been a subject of extensive studies due to intriguing interplay of the charge, orbital and spin degrees of freedom. The charge ordered (CO) state is formed due to localization of the mobile $e_g$-holes.

Above $T_{CO}$ the $e_g$-holes provide FM correlations between electron spins of neighboring manganese ions through the double-exchange (DE) mechanism proposed by Zener. Pr$_{1-x}$Ca$_x$MnO$_3$ (0.3 ≤ $x$ ≤ 0.75) oxides are the most suitable for investigation of the CO state since the onsets of the charge ($T_{CO}$) and spin ($T_N$) order are well separated in temperature. This doped oxide has an orthorhombic structure (space group, $Pbnm$) in a wide temperature and magnetic field ($< 20T$) range. It remains in the semiconducting state with no admixture of FM metal phase as opposed to Pr$_{1-x}$Sr$_x$MnO$_3$, La$_{1-x}$Ca$_x$MnO$_3$ and La$_{1-x}$Sr$_x$MnO$_3$. In the CO structure of Pr$_{1-x}$Ca$_x$MnO$_3$ with $x ∼ 0.5$ the in-plane pattern of Mn$^{3+}$ and Mn$^{4+}$ ions may be represented as a checkerboard related to the corresponding $t^3_2g^1$ and $t^3_g$ electronic configurations of Mn (Fig.1). The lobes of a certain number of occupied $e_g$-orbitals are ordered in the direction of the Mn$^{3+}$-O-Mn$^{4+}$ bond to maximize DE coupling. Whereas the AF superexchange $t_{2g} - t_{2g}$ coupling is a dominating magnetic interaction for Mn$^{4+}$ and Mn$^{3+}$ which $e_g$-lobes are aligned perpendicular to the Mn$^{3+}$-O-Mn$^{4+}$ bond. At $x ∼ 0.5$ the competition of these exchange couplings results in the AF spin ordering of CE-type with $T_N < T_{CO}$. The associated Jahn-Teller (JT) distortions of MnO$_6$ octahedra double the unit cell along b-axis of the orthorhombic ($Pbnm$) lattice. The ideal CE type charge/orbital order implies FM zigzag arrangement of the ordered $e_g(3x^2−r^2)$ and $e_g(3y^2−r^2)$ orbitals of Mn$^{3+}$ ions in ab-plane. The neighboring zigzags are AF-coupled, the ordering in c-direction is also antiferromagnetic.

Recent resonant x-ray scattering, electron microscopy and neutron diffraction studies of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ have shown that the orbital order (OO) below $T_N = 170K$ results in an orbital domain state commensurate with the lattice. This commensurate OO becomes metastable above $T_N$. Its melting is observed in diffraction studies as a commensurate-incommensurate (C-IC) transition at $T_{C-IC} ∼ (180−200)K > T_N$. With further increase of temperature the partial orbital disorder turns on the FM spin fluctuations which become dominating near $T_{CO} ∼ 250K$. The C-IC transition was considered in terms of the $e_g$-orbital polarization soft mode. The $e_g$-orbital completely polarized along Mn-O bond corresponds to the amplitude of the wave at a given Mn$^{3+}$ ion and its wave vector $q = \{0, 1/2−ε, 0\}$ was considered as the order parameter of the transition.

Further discussion of the CO state requires more detailed microscopic data related to the distribution of spin density and to its dynamic regime in the CO state of manganite. Studies of spatial fluctuations of charge/orbital order with diffraction experiments is restricted to short correlation times $τ_c < 10^{-12}s$. Whereas NMR experiments enable studying time-dependent spin fluctuations at much longer $τ_c$.

In this work we have studied the spin correlations of the neighboring Mn ions developed in the paramagnetic charge ordered (CO PM) state of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ by measuring the $^{17}$O NMR spectra. Oxygen atoms be-
ing placed between two Mn ions bring valuable information about the spin/orbital configuration of the nearest Mn ions. As expected the nuclear spin of oxygen \(^{17}\text{O} = 5/2\) probes its magnetic state through the dipolar and transferred hyperfine magnetic fields that depend on the spin/orbital configuration of the neighboring Mn ions. The \(^{55}\text{Mn}\) nucleus is a less suitable NMR probe for this task for the following reasons. First, the NMR spectrum of Mn\(^{3+}\) ion \((t^d_g\text{ electron configuration})\) is available only at low temperatures in the metastable CO AF phase. On the other hand, NMR of Mn\(^{3+}\)\((t^d_g\text{ electron configuration})\) is hard to detect due to extremely high nuclear spin-spin relaxation rate apparently controlled by abnormal low-frequency spin dynamic of the localized \(e_g\)-electrons.

This \(^{17}\text{O}\) NMR report is focused on the study of the development of the charge/orbital ordering in \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\). The main result is that in \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) the CE-type magnetic correlations develop gradually below \(T_{CO}\): first those between ab-layers arise and only at lower temperature the correlations within ab-planes appear. The static \((\tau_c > 10^{-4}s)\) orbital order is established only on approaching \(T_N\).

II. EXPERIMENTAL

We used a powder sample of \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) prepared by traditional ceramic technology. The powder was enriched with \(^{17}\text{O}\) isotope up to \(\approx 25\%\). The single-phase nature of the enriched sample was confirmed by the x-ray diffraction and Raman scattering studies at room temperature.

\(^{17}\text{O}\) NMR measurements were carried out on a phase-coherent NMR pulse Bruker spectrometer over the temperature range of \(80 - 330\text{K}\) in magnetic field of \(7T\). In this field the onset of the CO and AF spin ordering was found to shift slightly down to \(T_{CO} \approx 225\text{K}\) and \(T_N \approx 170\text{K}\) compared to reported data at zero field and in accordance with \(H\)-dependence of \(T_{CO}\) reported in Ref.\([8]\). NMR spectra were obtained for a loose-packed powder sample with point-by-point frequency sweep measurements, the intensity of the spin-echo signal formed with the pulse sequence \((\pi/2) - \tau_{del} - (\pi/2)\)-echo being measured. The width of the \(\pi/2\)-exciting pulse was \(\tau_p = (2 - 4.5)\mu\text{s}\) and the distance between pulses varied in the range of \(\tau_{del} = (40 - 80)\mu\text{s}\). For each frequency, the amplitude of the exciting rf-pulse was adjusted in order to optimize the echo signal intensity while keeping the pulse duration fixed. All the echo-intensities were corrected to \(\tau_{del} \approx 0\) by measuring the rate of echo-decay at different frequencies of the broad spectrum. All the spectra for \(T < T_{CO}\) were measured during cooling down from room temperature to avoid the hysteresis uncertainties. The \(^{17}\text{O}\) NMR signal in \(\text{H}_2\text{O}\) was used as a frequency reference to determine the shift of NMR line in our sample.

III. RESULTS AND DISCUSSION

A. The charge disordered paramagnetic state

Figure 2 shows the \(^{17}\text{O}\) NMR spectra of \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) measured in the PM state. In the charge disorder paramagnetic state (CD PM) for \(T > T_{CO} \approx 225\text{K}\) the main signal \((\sim 95\%)\) in the spectrum is a rather asymmetric line. It has a positive and extremely large magnetic shift exceeding 6\% even at the highest measured temperature, \(T = 330\text{K}\) with respect to those observed in nonmagnetic compounds. An additional line of small intensity \((\sim 5\%)\) is present at zero NMR-shift. It is supposed to originate from a small amount of the Ca-based oxides, which arise as spurious precipitations during the solid-state reaction synthesis. It's well known that a small concentration of spurious phase formed with light atoms like Ca is hard to detect by x-ray.

Let us now consider the quadrupolar and magnetic shift interactions of the oxygen nuclear spin with its environment. The oxygen atoms are located at the corners of octahedra with Mn at the center. The non-cubic local symmetry of oxygen sites leads to the interaction of \(^{17}\text{O}\) electric quadrupole moment \((eQ)\) with electric field gradient \((eV_{ZZ})\). The resulting \(^{17}\text{O}\) NMR spectrum is expected to split into \(2I + 1\) lines separated by the quadrupole frequency \(v_Q = e^2Q/2I(2I−1)\hbar V_{ZZ}\) at \(H \parallel O_Z\). Experimentally this characteristic first-order quadrupole splitting has never been observed. It shows that \(^{17}\nu_Q\) does not exceed the NMR linewidth measured at \(T = 330\text{K}\) i.e. \(v_Q < 1.4M\text{Hz}\) in agreement with Ref.\([10]\). Thus the quadrupolar interaction will only provide broadening effects on the observed pattern of NMR spectra, these quadrupolar effects being small compared to the magnetic interaction effects (see below).

The powder pattern spectrum of the \(\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3\) main line in the CD PM state may be described assuming an axial symmetry of the magnetic shift tensor \((K_\perp,K_\parallel,K_{||})\). The subscripts “ \(\perp\) ” or “ \(\parallel\) ” refer to the shift component \(K_\alpha\) of oxygen with Mn-O bond directed perpendicular or parallel to the external magnetic field \(H_0\), respectively. The analysis of the line leads to \(K_\perp = 7.0\%\) and \(K_{||} = 11.5\%\) at \(T = 295\text{K}\). The thermal variation of the shift is shown in Fig.3. With decreasing temperature the peak of the line is further shifted following the Curie-Weiss law with \(K = K_0 + a/(T−\theta)\). The corresponding fit curve drawn by a dashed line in Figs. 2-3 results in \(K_0 = -1.0(6)\%\) and \(\theta = 130(20)\text{K}\). A close value of \(\theta \approx 150\text{K}\) is obtained by fitting the magnetic susceptibility \((\chi)\) data measured in the range of \(T = 250 \div 300\text{K}\) in Ref.\([1]\). The positive value of \(\theta\) evidences that FM spin correlations between neighboring Mn are the dominating ones in the CD PM state above \(T_{CO}\). A similar conclusion about the prevalence of the FM spin correlations between Mn ions in the CD PM phase was inferred from the \(^{139}\text{La}\) NMR line shift in...
La_{0.5}Ca_{0.5}MnO_3, which becomes FM-metal in the field of 4T below $T \approx 220K$.

The slope of the $K$ vs $\chi$ plot corresponds to the local magnetic field $H_{loc} = \mu_B \Delta K/\Delta \chi \approx 1 \cdot 10^4 Oe/\mu_B$ (the $\chi$-data are taken from Fig.4 in Ref.[3]). It exceeds the magnitude of the classic dipolar field $(H_{dip})$ induced at oxygen by the magnetic moments of the neighboring Mn ions:

$$H_{dip} = \frac{2 g_e \mu_B \langle s_z(Mn) \rangle}{r_{Mn-O}^3} = \frac{2 \chi H}{r_{Mn-O}^4}. \quad (1)$$

At room temperature $H_{dip}$ may be estimated as $H_{dip} \approx 1200 Oe$ where $\chi$ is defined per spin from Ref.[3]. The corresponding estimated anisotropic contribution to the total NMR line shift $\{ -0.8%, -0.8%, 1.6% \}$ is much less than the experimental value. Thus we assume that the classic dipole interaction of $^{17}O$ nucleus with the effective magnetic moments $2g_e \mu_B \langle s_z(Mn) \rangle$ of the nearest Mn has no strong influence on the total shape of the spectrum.

The most probable origin of the observed giant isotropic magnetic shift $K_{iso} = (2K_{\perp} + K_{\parallel})/3$ is the Fermi contact interaction of the nuclear spin $^{17}I$ with the transferred $s$-spin density of electrons participating both in the Mn-O-Mn bonding and in superexchange coupling of the neighboring Mn,

$$K_{iso} = \frac{8 \pi}{3} g_e \mu_B |\phi_{2s}(0)|^2 \int f_s \langle s_z(Mn) \rangle = \frac{1}{17 \gamma h} a(2s) f_s \langle s_z(Mn) \rangle \quad (2)$$

Here $g_e \mu_B \langle s_z(Mn) \rangle = \chi H$, $a(2s) = \gamma h H_{FC}(2s) = 0.15 cm^{-1}$ is the isotropic hyperfine coupling constant for oxygen ion [12, 13]. $H_{FC}$ is the corresponding hyperfine magnetic field due to the Fermi-contact interaction with electron located on 2s-orbital with wave function $\psi_{2s}(r)$. Following [3, 9] the corresponding isotropic spin density transferred at oxygen from neighboring Mn ions may be defined in terms of the factor $f_s = H_{loc,iso}/2H_{FC}(2s)$. This quantity estimated from (2) results in a rather large magnitude of the effective fractional occupancy of O(2s) orbitals by unpaired spins. We found $f_s = 0.01$ for insulating PM state of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. For comparison the LDA+U band structure calculation results in $f_s = 0.003 - 0.007$ for the FM-ordered state of LaMnO$_3$ [14].

Another possible isotropic hyperfine interaction is the core-polarization term which provides $H_{iso} \approx 3 \cdot 10^4 Oe$ [14] when assuming that the doped electron is fully localized within the oxygen 2p-orbital. But this is not the case above $T_{CO}$ in Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. Thus this interaction may be neglected for the light oxygen atom.

The noncubic local symmetry of oxygen sites gives rise to an anisotropic part of the magnetic shift tensor $K_{ax} = (K_{\parallel} - K_{\perp})/3$. The most reasonable contribution to $K_{ax}$ is the magnetic dipole-dipole hyperfine interaction of $^{17}I$ with electrons on 2p$_{\sigma\pi}$ orbitals, which spin occupancies ‘up’ and ‘down’ become different through the polarizing interactions with neighboring manganese. The corresponding magnetic shift tensor $K_{dip}$ may be expressed through the fractional spin density transfer $f_a \langle s_z(Mn) \rangle$ on O-2p$_\sigma$ orbital from paramagnetic neighboring Mn-ion [3] as:

$$K_{\parallel}(2p_\sigma) = -2K_{\perp}(2p_\sigma) = \frac{4}{9} < r^{-3} > 2p f_a \chi(Mn); \quad (3)$$

$K_{\parallel}(2p_\sigma), K_{\perp}(2p_\sigma)$ being defined for $H_0$ parallel (perpendicular) to the Mn-O bond respectively. The resulting dipolar contribution to $K_{ax}$ is thus determined by the difference of transferred spin density $(f_{\sigma} - f_{\pi}) \langle s_z(Mn) \rangle$ for different O-2p orbitals from neighboring Mn-ion [3],

$$K_{ax} = \frac{2}{5} < r^{-3} > 2p (f_{\sigma} - f_{\pi}) \chi(Mn) \quad (4)$$

Taking $< r^{-3} > 2p = 4.97 a.u.$ [13] for neutral oxygen atom we obtain a rather large positive value $(f_{\sigma} - f_{\pi}) \approx 0.04$. The direct observation of the positive value of $(f_{\sigma} - f_{\pi})$ proves for the first time that the $p_\sigma$-orbital directed along the Mn-O bond is more polarized than the two other $p_\pi$-orbitals.

We showed before that the $^{17}O$ NMR line position in the CD PM state is mainly determined by the isotropic transferred hyperfine coupling, arising from the hybridization of Mn(3d) and O(2s) orbitals. In the ideal Pbnm structure there is no overlap of Mn(1z$_2$)-O(2s) orbitals due to their orthogonality, while $e_\sigma$-orbitals of Mn have a rather strong overlap with s-orbital of neighboring oxygen as shown in Fig.1. Hereafter we restrict ourselves to the effects of overlap and covalency between Mn($e_\sigma$) and O(2s) orbitals.

B. The charge ordered paramagnetic state

Just below $T_{CO}$ the $^{17}O$ NMR spectrum is substantially broadened. It splits into two parts as shown in Fig.2. The low-frequency spectrum in the range of $K = (-2.5 \pm 10%)$ is asymmetric (A-line). Its width decreases gradually as the temperature approaches $T_N$. The high-frequency spectrum is approximately twice larger in intensity and forms a rather complicated pattern which center of gravity is shifted to extremely large positive $K > 20\%$. At $T = 170 K \approx T_N$ it splits into two broad lines (B- and C-line) of about equal intensity and peaked at $K_B \approx 40\%$ and $K_C \approx 55\%$, respectively.

According to x-ray and neutron diffraction studies [3], the CO and OO of the CE-type becomes commensurate in the CO PM phase only near $T_N$. If the domain structure of the OO [3, 4] is ignored, one finds four groups of the oxygen atoms differentiated by the charge and/or by the direction of occupied $e_\sigma$-orbital of the nearest-neighboring Mn-ions. The first and the second groups are formed by apical oxygen located between two Mn$^{3+}$-ions (O1-site, shown in Fig.1) or between Mn$^{4+}$ (O2/O3-site), respectively. Note that the $s_z$-projections of electron spins are AF correlated for neighboring Mn from
adjacent ab-planes. A third group is formed by oxygen (O4) in the ab-plane which participates in the AF coupling of neighboring Mn\(^{4+}\), Mn\(^{3+}\) from adjacent zigzags. The last group (O5) is formed by oxygen in the ab-plane located between two FM coupled Mn\(^{4+}\) and Mn\(^{3+}\) ions inside a zigzag. The concentration of each type of oxygen atoms obeys the "structural" ratio 1 : 1 : 2 : 2.

In order to assign A-C-lines measured in the CO PM phase we analyze first the spectra near \(T_N\) with resolved structure. We compare the "structural" ratio with the experimental "NMR line intensity" ratio, which is close to 2 : 2 : 2. We also take into account that the local magnetic fields at different oxygen sites are formed through the Mn-O-Mn exchange interactions which are short-range in space. In CO PM phase the effective magnetic moment of Mn (shown in Fig.1 by arrows) is defined by its projection \(g_s\psi_B(s_z)\) on the direction of the external magnetic field. In turn it controls the sign of the corresponding \(^{17}\)O NMR shift contributed by each of the two neighboring Mn.

A-line is attributed to the apical (O1 and O2/O3) sites whereas B- and C-lines - to the in-plane ones. The magnetic shift of the A-line is small, and the local field at the corresponding \(^{17}\)O is comparable in magnitude to the classic dipolar field estimated above (1). At these apical sites the hyperfine magnetic shifts (2-4) are greatly reduced since both neighboring Mn-ions are in the same valence state and their effective magnetic moments \(g_s\psi_B(s_z)\) are AF correlated in the CO PM phase of CE-type.

Let us now consider the high-frequency part of the spectra. C-line demonstrating the largest positive shift may be attributed to oxygen positioned in O5 sites whereas B-line is presumably due to oxygen located in O4 sites. Indeed for oxygen in O5 site the transferred s-wave spin density is maximal since within the zigzag the lobe of the partially occupied \(e_g(m_l = 0)\) orbital of Mn\(^{3+}\) ion points toward the neighboring oxygen. Furthermore the two neighboring Mn ions are FM correlated. For O4 we definitely expect a rather large transferred hyperfine field for the following reason. Although the spins of Mn in adjacent zigzags are antiparallel, the O4 oxygen is "sandwiched" between Mn\(^{3+}\) and Mn\(^{4+}\) ions with different spin values and different orbital occupations, i.e. with different covalency. So that the transferred polarization from these two Mn ions should not compensate as they do for the apical oxygen (O1, O2/O3). This should again result in a substantial shift, although smaller than for O5. Moreover the transferred s-wave polarization from Mn\(^{4+}\) ion is expected to be negative due to effects of covalent mixing with the empty \(e_g\)-orbitals [18]. As reviewed in [18] the charge transfer from the occupied O-2s orbital to the empty eg-orbital is spin dependent. It is regulated by the intra-atomic exchange coupling with electrons on \(t_g\)-orbitals.

Thus in the CO PM phase the static s-wave polarization is directed along \(H\), and the isotropic shift at O5 site may be expressed similarly to (2) through the corresponding transferred spin densities \(f_{s,3+}\langle s_z(Mn^{3+})\rangle\) or \(f_{s,4+}\langle s_z(Mn^{4+})\rangle\) of the neighboring Mn (with \(f_{s,3+} > 0\) and \(f_{s,4+} < 0\)):

\[
K_{iso}(O5) = \frac{8\pi}{3} g_s \mu_B \psi_{2s}(0) \int_2 \{ f_{s,3+}\langle s_z(Mn^{3+})\rangle + f_{s,4+}\langle s_z(Mn^{4+})\rangle\} (5)
\]

The effective magnetic moments of neighboring Mn from adjacent zigzags are AF correlated and we obtain for \(K_{iso}(04)\) the following expression:

\[
K_{iso}(O4) = \frac{8\pi}{3} g_s \mu_B \psi_{2s}(0) \int_2 \{ 0.25 f_{s,3+}\langle s_z(Mn^{3+})\rangle - f_{s,4+}\langle s_z(Mn^{4+})\rangle\} \}
\]

The sign "+"/"-" in (5),(6) takes into account the fact that FM/AF spin correlations of the neighboring Mn\(^{4+}\) and Mn\(^{3+}\) ions are considered as static in the time interval which is much longer than the inverse splitting of the B- and C-line (~10\(^{-8}\)s) of the spectrum at \(T = 170K \approx T_N\), when the CO and OO are completely formed in PM state. This agrees with the fact that the O(2s)-polarization is provided predominantly by the \(\sigma\)-overlap with the \(e_g\)-orbitals of Mn, and Pauli blocking of part of \(e_g\)-orbitals in Mn\(^{3+}\) gives stronger polarization than in the case of Mn\(^{4+}\), where both 2\(\uparrow\) and 2\(\downarrow\) electrons of O2- may virtually hop to Mn\(^{4+}\) so that the net oxygen polarization due to covalency with Mn\(^{4+}\) will be smaller than for Mn\(^{3+}\)-neighbor and negative. For crude estimate of the transferred s-spin density we have assumed in (5),(6) that the \(\sigma\)-overlap of \(e_g(m_l = 0)\) orbital of Mn\(^{3+}\) with 2s-orbital of O5 in zigzag of the CE-type charge and orbital ordered phase is twice larger than the overlap with corresponding 2s-orbital of oxygen O4 located between the neighboring zigzags in ab-plane. (Of course under detailed consideration it should depend on interatomic distance and on the bending of the Mn\(^{3+}\)-O bond in the tilted and JT distorted MnO\(_6\) octahedra.) Inserting the value of the peak position of B-line (\(K_{iso} = 40\%) and C-line (\(K_{iso} = 55\%\)) into expressions (6),(5) respectively we get that the transferred s-wave polarization from Mn\(^{3+}\) ion is positive and its absolute value exceeds about 4 times the corresponding negative polarization transferred from Mn\(^{4+}\) |

The large difference in spin densities transferred from Mn\(^{3+}\)/Mn\(^{4+}\) ions indicates a substantial delocalization of the "\(e_g\)-hole" within the hybridized \(e_g(Mn^{3+})-2p_{\sigma}(O)\) orbital [19]. It shows that a pure ionic approach where the \(e_g\)-hole is completely localized at the Mn\(^{3+}\) ion is a very rough approximation to describe in detail the CO and OO in doped manganite.

Unfortunately the spatial distribution of the Fermi contact hyperfine fields results in a large broadening of the separate NMR lines in spectrum measured at \(T < T_{CO}\). It mask the anisotropy of the magnetic shift tensor and does not permit to trace the transfer of the 2p-spin density at oxygen in the CO PM phase, i.e. to address the orbital order more directly by studying polarization of a given p-orbital.
C. The antiferromagnetic state

Different local fields for apical oxygen in O1 and (O2/O3) sites are expected only in the spin-ordered phase below \( T_N \). In the AF phase the AF moment canting takes place when a rather high magnetic field (\( 7T \)) is applied. The canting moment of Mn in adjacent ab-planes will create at the apical oxygen an additional local field dependent on the valence state of neighboring Mn. At O1 sites the neighboring Mn\(^{3+}\) ions create a larger isotropic magnetic shift than Mn\(^{4+}\) ions do at O2/O3 sites. Indeed, as shown in Fig.4 at \( T = 100K \) A-line splits into two lines of roughly equal intensity. A loose packed powder sample in a strong enough external field may be considered as partially oriented with \( c \parallel H \). It should be noted that the observed splitting (4MHz) is not a result of the classic dipolar fields of the neighboring Mn ions since the difference in their effective magnetic moments is too small (\( \mu_{\text{eff}} = 2.7\mu_B \) for Mn\(^{3+}\) and 2.2\( \mu_B \) for Mn\(^{4+}\) as estimated from Fig.4 in Ref.[6]).

The only slight additional broadening of the NMR spectra even around \( T_N/2 \) evidences that the line shift is mainly determined by the short-range CO and OO which have been completely formed in the CO PM phase at \( T \to T_N \). Below 110K it appears that the optimal rf pulse duration increases about twice from the low to the high frequency part of the A-line as illustrated in Fig.5. The same feature was found for the high-frequency spectrum when the B- and C-lines are resolved. This striking effect of the nonmagnetic ligand atom on the echo formation may be related to a rather strong isotropic hyperfine interaction between \(^{17}O\) nuclear spin and the Mn electron spin system with long-range AF spin order. The detailed analysis of the spectra measured below \( T_N \) requires additional studies which are now in progress.

D. Development of charge and orbital ordering

Based on the site assignment considered above we propose the following picture of the development of spin correlation in the Pr\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) CO PM phase as seen by \(^{17}O\) NMR. In the low-temperature part of the CO PM phase the NMR spectrum represents the spin density distribution on oxygen ions. Its value is determined not just by the Mn effective magnetic moment but, to a greater extent, by the type of spin correlations of the neighboring Mn atoms. The presence of several lines in NMR spectrum, which can be attributed to the various oxygen sites in the lattice, shows that the corresponding spin correlations and effective magnetic moment of the neighboring cations do not change at the time scale \( t \geq 10/(\Delta \omega) \approx 10^{-6}s (\Delta \omega = \text{line splitting}) \). The thermally activated hopping of \( e_g \)-holes seems to be the main mechanism changing the charge state of the ion (Mn\(^{3+}\)-Mn\(^{4+}\)) and the spin correlations between the neighboring ions, which results in the “melting” of OO in CO PM phase. With increasing temperature the line structure of the spectrum is smeared as the corresponding correlation time (\( \tau_c \)) of the specific hoping becomes comparable with (\( \Delta \omega \))\(^{-1} \). As a result the various spin configurations are no more distinguishable at higher temperature.

The splitting of the NMR spectrum just below \( T_{CO} \) into the A- and (B+C)-lines may be explained as follows. As has been mentioned above the oxygen nuclei responsible for A-line are located between two AF correlated Mn ions from adjacent ab-plane whereas those responsible for (B+C)-line have two neighboring Mn ions in the same ab-plane. The resolution of A-line shows that just below \( T_{CO} \) the correlation time of the AF correlated spin of neighboring Mn from adjacent ab-planes becomes long compared to the NMR time scale. By contrast (B+C)-line is still unresolved just below \( T_{CO} \). Thus in the first stage of the charge ordering the three-dimensional (3D) motion of eg-electrons transforms preferentially into a two-dimensional (2D) hopping within the ab-planes. Such an ordering phase transition may be considered as the nucleation of AF ordered clusters which grow at the expense of the CD PM phase which dominates above \( T_{CO} \). Furthermore as the temperature decreases and the unresolved (B+C)-line is shifted toward high frequency a shoulder appears on the low frequency part (see spectra for \( T \approx 200K \) at Fig. 2). The temperature dependence of this signal follows the same Curie-Weiss law as the peak in the CD PM phase (dashed line in Figs. 2, 3). Its relative intensity decreases with temperature and becomes negligible only near \( T_N \). This may indicate that almost down to \( T_N \) traces of the CD PM phase remain in the CO PM phase.

The proposed NMR interpretation of the ordering in the CO PM phase is in a good agreement with the main results of the resonant x-ray \(^{\text{[4]}}\) and neutron diffraction studies \(^{\text{[5]}}\). It should be noted that the time scales required to get a quasi-static picture of charge distribution in NMR (\( t_{\text{nmr}} > 10^{-6}s \)) and in neutron diffraction (\( t_{\text{nd}} \sim 10^{-12}s \)) experiments are very different. Both methods confirm the presence of FM correlations between Mn as dominant spin fluctuations in the CD PM phase which reduce in intensity below \( T_{CO} \). In the neutron scattering experiments the short-range FM correlations are considered as a static whereas it is seen still as a low-frequency dynamic phenomenon in the NMR spectra. In conclusion, the distribution of spin density and the development of the charge and orbital ordering in the paramagnetic state of Pr\(_{0.5}\)Ca\(_{0.5}\)MnO\(_3\) were studied for the first time by means of \(^{17}O\) NMR. It is shown that the main interaction of oxygen is the isotropic hyperfine Fermi-contact interaction with the s-electron spin density transferred from the nearest-neighbor Mn ions. The resulting magnetic line shift is very sensitive to both the electronic configuration of the neighboring cation (Mn\(^{3+}\)/Mn\(^{4+}\)) and to their specific spin-pair correlations that develop on cooling in the charge and orbital ordered PM phase. It is shown that with increasing temperature the melting of the orbital ordering first develops within the ab-plane whereas the AF correlations between Mn
ions in adjacent layers are more stable and disappear only when $T$ approaches $T_{CO}$.

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FIG. 1: Charge and orbital-ordered Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ with CE-type magnetic structure: ● - Mn$^{4+}$-ions; ○ - Mn$^{3+}$-ions with occupied $e_g$-orbitals; ◦ - oxygen ions (O1-O5). The CE-type of spin correlations in the charge ordered paramagnetic phase is shown by arrows directed up/down relative to the applied magnetic field $H$$\parallel$$c$.
FIG. 2: $^{17}$O NMR spectra measured at $H = 7T$ in the paramagnetic state of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$. The dashed line represents the fitting curve of the line peak shift by the expression $K_0 + a/(T - \theta)$ for spectra measured above $T_{CO}$.

FIG. 3: a) The line peak shift $K$ (solid squares) and $K_\perp$ (solid circles) vs. $T$ plot. The dashed curve is the fit of $K$ data by the expression $K_0 + a/(T - \theta)$ with $K_0 = -1.0(6)\%$ and $\theta = 130(10)K$ for spectra measured above $T_{CO}$; solid line represents the fitting curve of the line peak shift by the expression $K_0 + a/(T - \theta)$; b) Relative $^{17}$O NMR line intensity of oxygens in the charge disordered regions of PM phase.
FIG. 4: $^{17}$O NMR spectra measured at $H_{ext} = 7T$ in the AF phase of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$.

FIG. 5: Evolution of the echo-spectra shape of A-line measured with different rf-pulse durations ($t_p$) at $T = 100K$ in the AF phase.