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Experimental evidence for the mechanism of successive magnetic phase transitions in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$

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Abstract. ^{139}La zero-field NMR measurements and NMR measurements under external magnetic fields in the layered perovskite compound $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ ($x = 0-1.3$) have been carried out at low temperatures. With the Sr substitution three different ^{139}La resonances were observed as follows. In the antiferromagnetic (AF) state for $0 \leq x \leq 1.0$,

(i) zero-field NMR with a large internal magnetic field of ~ 18 kOe, whose intensity decreases linearly with x up to $x = 1.0$ and

(ii) NMR with $K \sim 0$ Knight shift and broad line-width (~ 4 kOe for $x = 0.9$), whose intensity increases rapidly in the region close to $x = 1.0$.

In the regions close to $x \sim 0$ and to $x \sim 1.0$, the relaxation rate T_1^{-1} of ^{139}La zero-field NMR and NMR under an external field is proportional to $T^{2.6}$ and to $T^{-2.7}$, respectively, corresponding to the 3D long-range order of antiferromagnetism (LOAF). In the paramagnetic state for $x > 1.0$,

(iii) NMR with $K \sim 0$ but rather sharp line-width (~ 2 kOe for $x = 1.3$). T_1^{-1} follows a Korringa-like relation, $T_1 T = \text{constant}$, indicating a metallic state.

We concluded that in the insulative AF region ($0 \leq x \leq 1.0$) the doped holes occupy mainly the Ni $3d_{x^2-y^2}$ orbital and, with increasing x , the LOAF state at $x \sim 0$ associated with Ni^{2+} ($S = 1$) spins translates to the LOAF state at $x \sim 1.0$ with Ni^{3+} ($S = \frac{1}{2}$) spins. On further substitution of Sr above $x \gtrsim 1.0$, the excess holes should go into the O $2p_{x,y}$ orbital in the Ni–O plane through the Ni $3d_{x^2-y^2}$ orbital, giving rise to the spin frustration of the Ni^{3+} ($S = \frac{1}{2}$) spins.

1. Introduction

Recently considerable experimental and theoretical attention have been concentrated on the layered perovskite compounds La_2MO_4 ($M=3d$ transition-metal atoms), related to the family of high- T_c cuprate compounds, because the La_2MO_4 series has been found to be a good candidate to study systematically the effect of the 3d-electron correlation strength on characteristic properties such as the metal–insulator transition, magnetism, superconductivity and so on. This is due to mainly the fact that one can control the initial 3d-electron (hole) number, excess hole doping and two dimensionality without changing the K_2NiF_4 -type crystal structure.

All the hole non-doped samples, La_2CuO_4 (Cu^{2+} : $3d^9$, $S = \frac{1}{2}$), La_2NiO_4 (Ni^{2+} : $3d^8$, $S = 1$) and La_2CoO_4 (Co^{2+} : $3d^7$, $S = \frac{3}{2}$) are antiferromagnetic (AF) insulators [1–3]. A significant effect of the difference in the initial hole number appears in the successive phase transitions at low temperatures when excess holes are introduced by Sr substitution for La: $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ goes into the superconducting (SC) state at $x \sim 0.05$ and to the paramagnetic

metal (PM) state at $x \sim 0.3$ [4], $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ to PM at $x \sim 1.0$ [5] without SC appearance, and $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ to the ferromagnetic state at $x \sim 0.6$ and to the paramagnetic state at $x \sim 1.1$ [6].

There is particular interest in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ at $x \sim 1.0$ since the formal valence of Ni^{+3} (d^7) could take a low-spin configuration with $S = \frac{1}{2}$, equivalent to the $S = \frac{1}{2}$ spin state of Cu^{2+} in the high- T_c cuprate mother compound. An analysis of the iodometric titration by Kato *et al* [7] indicated that, on increasing x from 0 to 1.0, the valence number of Ni changes from +2 to +3. Demazeau *et al* [8] carried out an EPR experiment and concluded that Ni^{3+} is in the low-spin configuration. Kato *et al* [9] found the presence of a broad peak at $x \sim 1.0$ in the temperature dependence of magnetic susceptibility, characteristic of the two-dimensional AF correlation.

In order to understand the mechanism of the phase transition in the Sr-doped La_2NiO_4 , however, it is important to know microscopically how the doped holes distribute to Ni 3d orbitals and/or O 2p orbitals over the initial hole occupation: for Ni^{2+} both $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals are occupied by approximately one hole each with parallel spins. From the x dependence of lattice parameters, Cava *et al* [10] suggested that the doped hole primarily goes into the $3d_{z^2}$ orbital up to $x \sim 0.5$ and then into the $3d_{x^2-y^2}$ orbital. An analysis of the magnetic susceptibility data [9] indicated that the doped hole occupies mainly the $3d_{z^2}$ orbital. In contrast, a photoemission spectroscopy study [11] concluded that the doped holes have mainly the O 2p character as in the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [12], although the 3d character of the doped holes is much larger in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ than in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$.

In the present study of ^{139}La zero-field nuclear magnetic resonance (zero-field NMR) and nuclear magnetic resonance (NMR) under an external field in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$, we have obtained experimental evidence for the doped hole occupying the $3d_{z^2}$ orbital up to $x \sim 1.0$, giving rise to an $S = \frac{1}{2}$ long-range AF order in the region close to $x \sim 1.0$. On further substitution of Sr, exceeding $x \sim 1.0$, the doped hole would consequently occupy the $2p_{x,y}$ orbital of O, which is hybridized strongly with the Ni $3d_{x^2-y^2}$ orbital. This causes the abrupt transition from the insulative AF state with $S = \frac{1}{2}$ to the PM state.

2. Experimental results and analysis

2.1. Magnetization

The samples of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ compounds ($x = 0-1.3$) were prepared by the standard solid-state reaction method and annealed in air. X-ray powder diffraction patterns at room temperature show that all the samples are in a single phase of tetragonal structure ($I4/mmm$). The dependence of c and a lattice parameters on the Sr content [5, 13] agrees qualitatively with that reported by Takeda *et al* [14].

The magnetic susceptibility χ of the samples with $x = 0-1.3$ showed almost the same temperature dependence as reported by Cava *et al* [10]. The magnitude of χ both at 4.2 K and at 300 K decreases monotonically with increasing x up to $x \sim 1.0$. We also measured the magnetization M as a function of the external magnetic field H at 4.2 K. As typically shown in figure 1 for $x = 0.5$ and $x = 1.0$, with increasing H , M increases linearly. The sample with $x = 0.5$ shows a considerable extent of residual magnetization at $H = 0$, suggesting the existence of a weak ferromagnetization. The inset in the figure shows the dependence of the residual magnetization $M(H = 0)$ on x at 4.2 K, which takes a sharp maximum at $x = 0.5$.

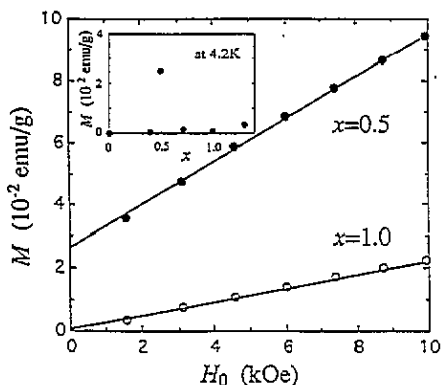


Figure 1. The dependence of the magnetization in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ on the external magnetic field at 4.2 K: closed circles, $x = 0.5$; open circles, $x = 1.0$. The inset shows the x dependence of the residual magnetization $M(H = 0)$ at 4.2 K.

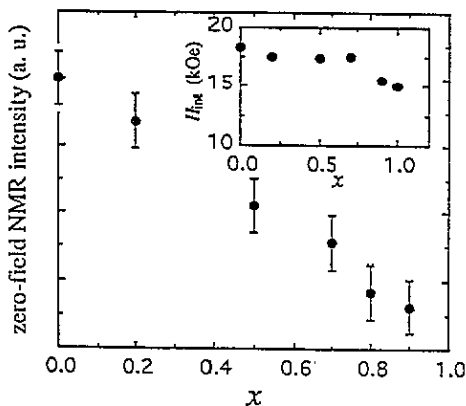


Figure 2. The dependence of the ^{139}La zero-field NMR intensity on the Sr concentration x in the AF state in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ at 1.4 K. The inset shows the x dependence of H_{int} at the La site.

2.2. ^{139}La zero-field nuclear magnetic resonance

2.2.1. Spectrum. ^{139}La zero-field NMR experiment has been carried out using a coherent-type spin-echo NMR spectrometer in the temperature range of $T = 1.4\text{--}4.2$ K. In the AF state, ^{139}La zero-field NMR spectra were observed, where the energy splitting of the nuclear-spin level of La atoms is dominated by the internal magnetic field originating from the Ni spins as reported in [13]. Figure 2 shows the x dependence of the zero-field NMR intensity in the AF region of $x = 0\text{--}1.0$ at 1.4 K. Here the observed intensity was normalized by the number of La nuclei in the sample, by longitudinal and transverse relaxation times and by the resonance frequencies. The inset in figure 2 shows the x dependence of the internal magnetic field H_{int} at the La site reported in our previous papers [5, 13]. With the increase of x , the zero-field NMR intensity decreases linearly but $H_{\text{int}} \sim 18$ kOe originating from the Ni^{2+} ($S = 1$) spin hardly changes up to $x \sim 1.0$. These results indicate that the number of La nuclei with the internal magnetic field associated with the Ni^{2+} spin decreases linearly with increasing x .

2.2.2. Spin-lattice relaxation time T_1 . To investigate dynamical properties of Ni^{2+} spins in the AF state, we have measured the temperature dependence of T_1 of the ^{139}La zero-field NMR for the samples with $x = 0\text{--}0.9$. T_1 for $x = 0$ and 0.2 was obtained by the ordinary single-saturation-RF-pulse method.

For $x = 0$, as reported previously [13], T_1^{-1} is extremely small at low T ($\sim 6.7 \times 10^{-3} \text{ s}^{-1}$ at 4.2 K) and proportional to $T^{2.6}$, corresponding to a three-dimensional (3D) long-range order of antiferromagnetism (LOAF) [15, 16]. For $x = 0.2$, T_1^{-1} is strongly enhanced ($\sim 14 \text{ s}^{-1}$ at 4.2 K) and the power of T diminishes drastically ($T_1^{-1} \propto T^{-0.7}$). A similar augmentation of the T_1^{-1} value with Sr substitution was also observed in the $\text{La}_{2-x}\text{Sr}_x\text{CoO}_4$ compound [6].

For $x \geq 0.5$, the zero-field NMR intensities were too poor to deduce an accurate value of T_1 by the saturation-pulse method for the T_1 measurement. Then we tried to estimate the value of T_1 from the temperature dependence of the transverse relaxation time T_2 , utilizing

the relation [17]

$$1/T_2(T) = 1/T_2^* + a/T_1(T) \quad (1)$$

where T_2^* is the T -independent spin-spin relaxation time and was negligibly small in the present case. The experimental T_2 is defined as

$$M(2\tau) = M(0) \exp(-2\tau/T_2) \quad (2)$$

where $M(2\tau)$ is the spin-echo intensity focused at a time 2τ after the application of $\pi/2-\pi$ RF pulses separated by τ . Figure 3 shows a typical spin-echo decay behaviour of ^{139}La observed in the sample with $x = 0.5$ at 1.4 K (\circ), 2.8 K (\square) and 4.2 K (\triangle). The value of $M(0)$ at 1.4 K was obtained by a smooth extrapolation of the decay data to $\tau = 0$, and $M(0)$ for higher temperatures was estimated assuming that $M(0)$ varies in proportion to $1/T$. As can be seen in the figure, the experimental data cannot be reproduced by (2), indicating that there is a distribution of T_2 value in the observed ^{139}La magnetization. Then tentatively we took three characteristic time constants $T_{1/10}$, $T_{2/10}$ and $T_{4/10}$, where $M(2\tau)$ decays to $\frac{1}{10}$, $\frac{2}{10}$ and $\frac{4}{10}$ of $M(0)$, respectively. For the samples with $x = 0.2$ and 0.5 , we confirmed that each time constant gives almost the same T dependence within our experimental uncertainty. Thus we found that, for $x = 0-0.9$, the T dependence of $(T_{1/10})^{-1}$ is roughly proportional to T^α in the range of $T = 1.4-4.2$ K.

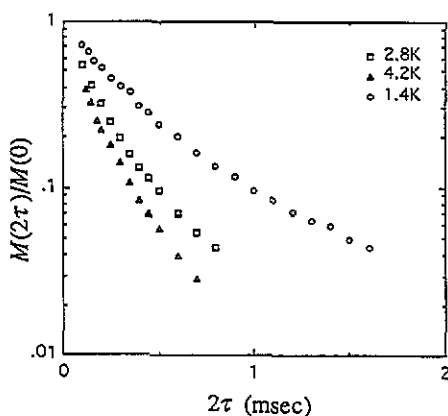


Figure 3. Typical spin-echo decay curves of ^{139}La magnetization for $x = 0.5$: \circ , 1.4 K; \square , 2.8 K; \triangle , 4.2 K.

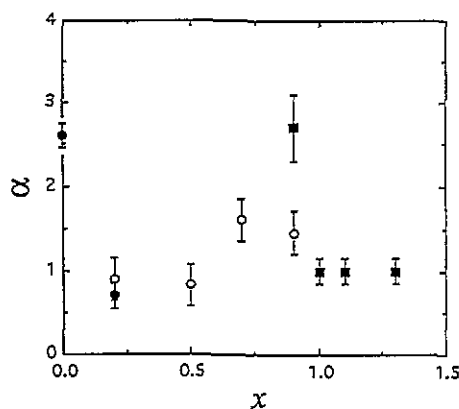


Figure 4. The power dependence of ^{139}La T_1^{-1} on T , $T_1^{-1} \propto T^\alpha$, observed in the temperature range of $T = 1.4-4.2$ K: \bullet , α obtained by T_1 measurement in ^{139}La zero-field NMR; \circ , α deduced from the temperature dependence of T_2 through the procedure described in the text; \blacksquare , α obtained by T_1 measurement in ^{139}La NMR.

The open circles in figure 4 show the x dependence of α obtained through these procedures. The value of $\alpha = 0.9$ (\circ) for $x = 0.2$ is not very far from $\alpha = 0.7$ (\bullet) obtained by the T_1 measurement described above. With Sr substitution, α shows initially an abrupt drop and then a monotonic increase up to $x \sim 1.0$.

2.3. ^{139}La nuclear magnetic resonance under external magnetic field

2.3.1. *Spectrum.* Figure 5 shows the NMR spectra observed for the samples with $x = 0.7, 0.9, 1.0$ and 1.3 at 1.7 K and 22 MHz as a function of the external magnetic field H . The Knight shift, K , is almost zero and independent of the Sr content, x . The inset in the figure shows the x dependence of the NMR intensity, normalized by a similar procedure as in the case of zero-field NMR intensity. An abrupt increase of the ^{139}La NMR intensity and significant narrowing of the line-width are observed with the increase of x through $x \sim 1.0$.

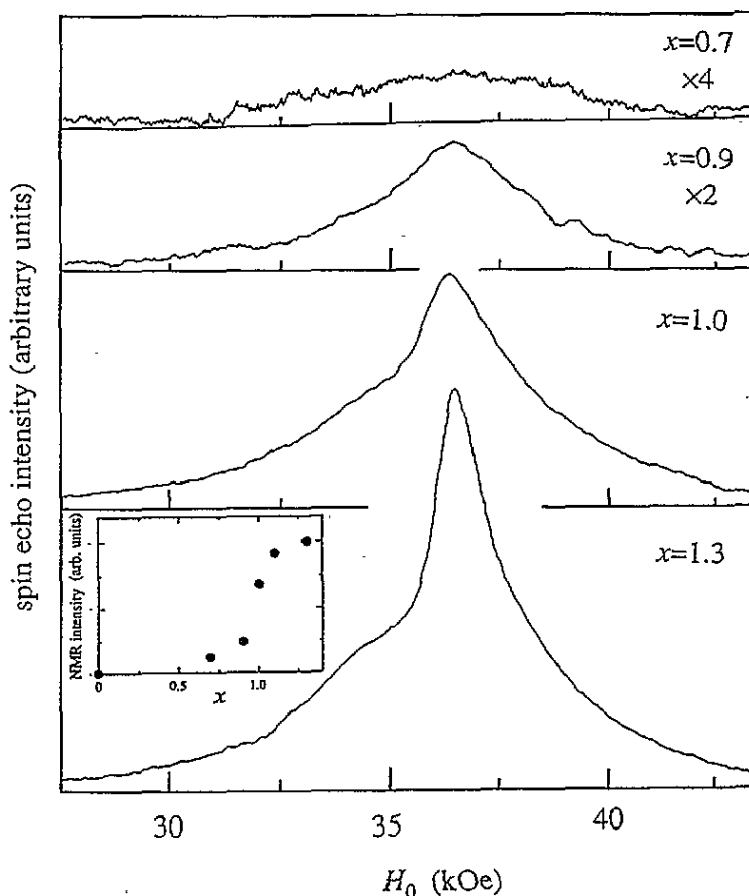


Figure 5. ^{139}La NMR spectra in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ with $x = 0.7, 0.9, 1.0$ and 1.3 observed at 1.7 K and $\nu = 22\text{ MHz}$. The inset shows the x dependence of ^{139}La NMR intensity at 1.7 K .

2.3.2. *Spin-lattice relaxation time T_1 .* T_1 of ^{139}La NMR at 22 MHz was measured at the peak intensity point of the spectrum. In the case of ^{139}La ($I = \frac{7}{2}$), the magnetization recovery of the central $|\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ transition after a $\pi/2$ RF saturation pulse is given by [18]

$$\frac{[M(\infty) - M(t)]}{M(\infty)} = 0.013 e^{-2Wt} + 0.068 e^{-12Wt} + 0.206 e^{-30Wt} + 0.714 e^{-56Wt} \quad (3)$$

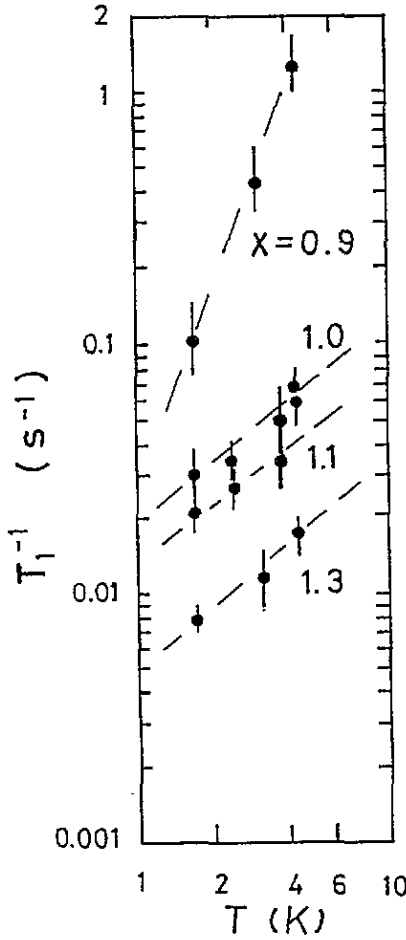


Figure 6. Temperature dependences of $T_{1(s)}^{-1}$ of ^{139}La NMR in $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$.

where $M(t)$ is the magnetization at a time t after the saturating pulse and $2W = T_1^{-1}$. The equation, however, could not fit the experimental data. Then we tentatively assumed that the experimental recovery curve is composed of two components with slow and fast relaxation rates, $2W_s = T_{1(s)}^{-1}$ and $2W_f = T_{1(f)}^{-1}$, respectively; we carried out a fit using the following equation:

$$\frac{[M(\infty) - M(t)]}{M(\infty)} = M_s[0.013 e^{-2W_s t} + 0.068 e^{-12W_s t} + 0.206 e^{-30W_s t} + 0.714 e^{-56W_s t}] + M_f[0.013 e^{-2W_f t} + 0.068 e^{-12W_f t} + 0.206 e^{-30W_f t} + 0.714 e^{-56W_f t}] \quad (4)$$

where $M_s + M_f = 1$ and M_s gives the content of the slow relaxation component. Taking W_s , W_f and M_s as adjusting parameters, we obtained a better fit.

Figure 6 shows the temperature dependence of $T_{1(s)}^{-1}$ in the range of $T = 1.7\text{--}4.2$ K. The temperature dependences of $T_{1(f)}^{-1}$ are almost the same as those of $T_{1(s)}^{-1}$ and the ratio $M_s/M_f \sim 0.25$ hardly depends on the Sr concentration or the temperature. As typically

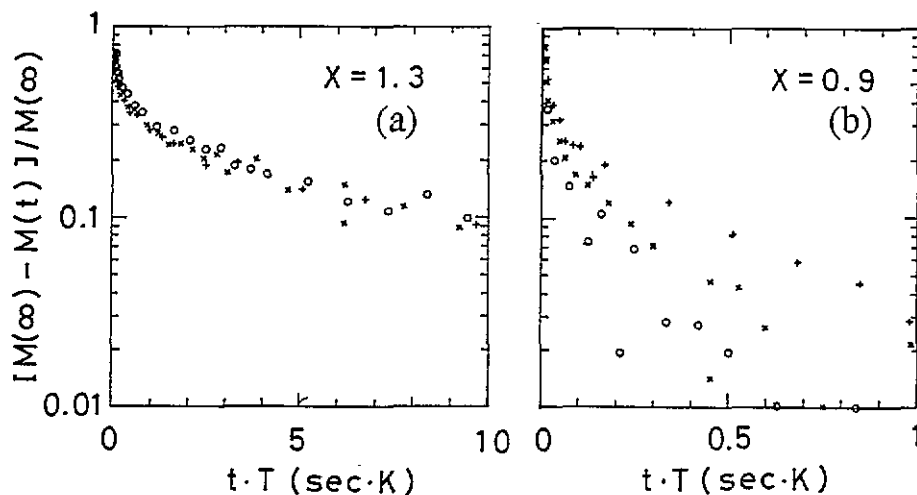


Figure 7. The recovery behaviour of ^{139}La magnetization, $[M(\infty) - M(t)]/M(\infty)$ plotted against tT : (a) for $x = 1.3$; (b) for $x = 0.9$; \circ , 4.2 K; \times , 3.1 K; $+$, 1.7 K. The experimental uncertainty of each data point is ~ 0.01 .

shown in figure 7(a) for $x = 1.3$, $[M(\infty) - M(t)]/M(\infty)$ at 1.7 K, 3.1 K and 4.2 K plotted against tT is on the same recovery curve for $x = 1.0, 1.1$ and 1.3. Thus, for $x \geq 1.0$, we may conclude that T_1 roughly follows the Korringa-like relation of $T_1T = \text{constant}$ and the systems are in a metallic state. The values of $T_{1(s)}T$ are ~ 56 s K, ~ 77 s K and ~ 208 s K for $x = 1.0, 1.1$ and 1.3, respectively. The ratio W_f/W_s is $\sim 51, \sim 35$ and ~ 35 , for $x = 1.0, 1.1$ and 1.3, respectively. For $x = 0.9$, on the other hand, T_1^{-1} does not follow the $T_1T = \text{constant}$ relation, as shown in figure 7(b), but varies as $T^{-2.7}$.

We have to note that the present values of T_1T obtained at 22 MHz (36.5 kOe) for $x \geq 1.0$ are larger than the values obtained at 6 MHz (9.9 kOe) reported in [5]. The ratio $(T_1T(22 \text{ MHz}))/T_1T(6 \text{ MHz})$ is ~ 7.3 for $x = 1.0$ and ~ 4.3 for $x = 1.3$.

Under the low external magnetic field of ~ 10 kOe, one would have to take the effect of the quadrupole splitting ν_Q on the relaxation rate for the $|\frac{1}{2}\rangle \leftrightarrow |-\frac{1}{2}\rangle$ transition into account. If we tentatively use a value of quadrupole interaction $\nu_Q = 2.6$ MHz in the tetragonal phase of $\text{La}_2\text{NiO}_{4+\delta}$ [13], the ratios of the decay constant corresponding to $2W$ and $56W$ in (3) are obtained as

$$\frac{2W(22 \text{ MHz})}{2W(6 \text{ MHz})} \sim 0.79 \quad \frac{56W(22 \text{ MHz})}{56W(6 \text{ MHz})} \sim 0.90 \quad (5)$$

by a straightforward calculation of the rate equations. Thus this cannot explain the experimental $(T_1T)^{-1}$ enhancement appearing at low H .

3. Discussion

We first review briefly the NMR characteristics in La_2NiO_4 ($x = 0$) to facilitate understanding of the subsequent discussion (details are presented in [13]). In $\text{La}_2\text{NiO}_{4+\delta}$, the configuration of Ni^{2+} is $3d^8$, and both the $3d_{x^2-y^2}$ and the $3d_{z^2}$ orbitals are occupied by one hole with parallel spins as illustrated in figure 8(a). The internal field H_{int} at the La site is 17.8 kOe in

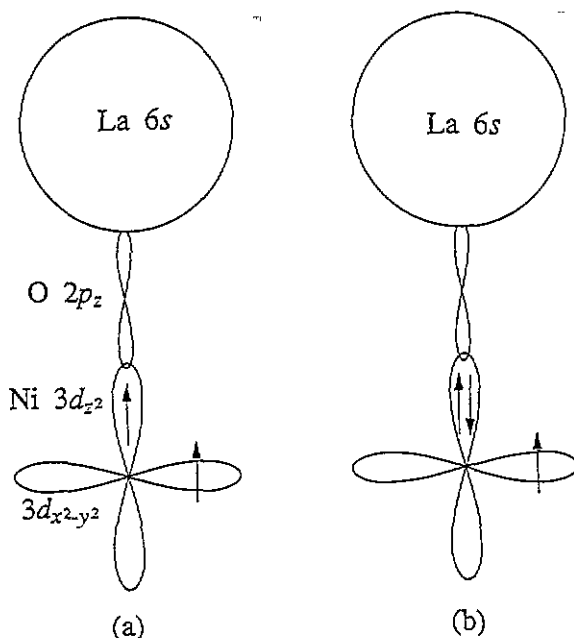


Figure 8. An illustration of the hole distribution, shown by arrows, on Ni orbitals: (a) the Ni^{2+} ($S = 1$) configuration, giving rise to a strong transferred exchange interaction between Ni $3d_{z^2}$ and La $6s$ orbitals through the $2p_z$ orbital of apical O; (b) the Ni^{3+} ($S = \frac{1}{2}$) configuration, where the transferred exchange interaction is almost quenched.

the AF state for the tetragonal crystal structure [13]. The large H_{int} could not be explained at all by the dipole field caused by the Ni^{2+} moment of $1.6\mu_B$ [19], but by the strong transferred exchange interaction between the Ni $3d_{z^2}$ orbital and the La $6s$ orbital through the $2p_z$ orbital of apical O [20]. Here, the existence of the half-filled $3d_{z^2}$ orbital plays an important role in the transferred exchange interaction.

3.1. Occupation of the doped hole in the insulative AF region

With Sr substitution for La in $\text{La}_2\text{NiO}_{4+\delta}$, we have found that the number of La nuclei with large H_{int} decreases linearly with increasing x without any significant variation of H_{int} up to $x \sim 1.0$. In the Sr concentration range of $0 \leq x \leq 1.0$, the resistivity at low temperatures increases insulatively with decreasing T [14]. Thus the doped holes should be localized and are considered to change from the Ni^{2+} ion ($S = 1$) to the Ni^{3+} ion with the low-spin configuration ($S = \frac{1}{2}$). In this ionic picture, the ratio of $\text{Ni}^{2+}/\text{Ni}^{3+}$ approaches unity at $x = 0.5$. Then one may expect that the system at $x = 0.5$ is in a ferrimagnetic-like state in which Ni^{2+} ($S = 1$) and Ni^{3+} ($S = \frac{1}{2}$) are arrayed alternately with antiparallel spin directions. A weak ferromagnetic component observed in the magnetization measurement, which takes a sharp maximum at $x = 0.5$, may correspond to this ferrimagnetic-like spin state.

If the doped hole occupied the Ni $3d_{x^2-y^2}$ orbital or the O $2p_{x,y}$ orbital in the Ni–O plane, which is hybridized strongly with the $3d_{x^2-y^2}$ orbital, the occupation of the $3d_{z^2}$ orbital by one hole would not change. Thus the transferred exchange interaction between the Ni $3d_{z^2}$ and the La $6s$ orbitals through the $2p_z$ orbital of the apical O remains unchanged [20] and H_{int} keeps its initial value of ~ 18 kOe at $x = 0$. In our preceding paper [13] we

falsely concluded this. If this were the present case, however, the number of La nuclei with large H_{int} would not vary with the Sr doping, contradicting the experimental linear decrease in the ^{139}La zero-field NMR intensity shown in figure 2.

If the doped hole occupied the Ni $3d_{z^2}$ orbital, on the other hand, the orbital would be almost empty and, therefore, the transfer probabilities of the electrons with up and down spin from the apical O to the $3d_{z^2}$ orbital would be nearly equalized. Then the occupation of the doped hole on the $3d_{z^2}$ orbital would result in a quenching of the transferred exchange interaction (refer to figure 8(b)), giving rise to a very small internal magnetic field at La nuclei. As the ^{139}La resonance signal with small H_{int} is hard to detect by zero-field NMR measurement, the linear increase of the Ni^{3+} ions with Sr doping should result in a linear decrease in the ^{139}La zero-field NMR intensity with large H_{int} , in agreement with the present zero-field NMR experimental results. Thus we concluded that *the doped holes occupy the Ni $3d_{z^2}$ orbital up to $x \simeq 1.0$ and quench the transferred exchange interaction between the La and Ni atoms.*

3.2. Magnetic order of Ni^{3+} ($S = \frac{1}{2}$) spins in the region close to $x < 1.0$

Now we focus our interest on magnetic states associated with Ni^{3+} ($S = \frac{1}{2}$) ions at $x \leq 1.0$, where most of the Ni atoms are considered to be Ni^{3+} ions with the $S = \frac{1}{2}$ low-spin configuration.

In the Sr concentration range of $x \simeq 0.7 \sim 1.0$, we found ^{139}La NMR with almost zero Knight shift, though the system is still in the AF and insulative state. The broad line-width (~ 4 kOe for $x = 0.9$) decreases drastically when the system goes into the PM state through $x = 1.0$. As shown in figure 7, T_1^{-1} of ^{139}La NMR for $x = 0.9$ is proportional to $T^{-2.7}$, which is close to the $T^{2.6}$ dependence in the LOAF state of La_2NiO_4 [13]. These results indicate that $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ in the region close to $x \sim 1.0$ is in a LOAF state associated with Ni^{3+} ($S = \frac{1}{2}$) spins.

For the case of Ni^{3+} with the empty $3d_{x^2-y^2}$ orbital, the transferred exchange interaction is almost quenched. The magnetic dipole field at the La site originating from the Ni^{3+} ($S = \frac{1}{2}$) magnetic moment ($\sim 1\mu_B$) is evaluated to be ~ 1 kOe. Thus the ^{139}La NMR line-width of ~ 4 kOe for the powder sample of $x = 0.9$ and 1.0 under the external magnetic field is considered to be composed of the dipole magnetic broadening (~ 2 kOe) and the electric quadrupole broadening (~ 2 kOe). The significant broadening of NMR line-width with decreasing x below $x \sim 0.9$ would be caused by the increase of the Ni^{2+} ($S = 1$) spins.

Following our consideration described above, the ^{139}La NMR intensity associated with the Ni^{3+} ($S = \frac{1}{2}$) spin should be proportional to x . As shown in figure 5, however, the NMR intensity seems to drop more rapidly on decreasing x from $x = 1.0$. The lack of the total NMR intensity in the small- x region is due to the missing of the weak signal at the tail parts of the spectrum because of the severe broadening of the ^{139}La NMR spectrum.

Thus we may conclude that, *in the range close to $x \sim 0$, the system is in the LOAF state associated with Ni^{2+} ($S=1$) and, in the range close to $x \sim 1.0$, the system is in the LOAF state associated with Ni^{3+} ($S = \frac{1}{2}$).*

In the intermediate region between $x \sim 0.2$ and $x \sim 0.7$, where the Ni^{3+} and Ni^{2+} ions distribute randomly, the long-range order of both the Ni^{2+} ($S = 1$) spins at $x = 0$ and Ni^{3+} ($S = \frac{1}{2}$) spins at $x = 1.0$ is considered to be broken. As shown in figure 4 the power dependence of T_1^{-1} on T , α , decreases from ~ 2.7 for LOAF down to ~ 0.7 in the intermediate AF region, which is indicative of the destruction of the long-range order. This is expected from the fact that one can observe a T -independent T_1^{-1} in an extreme

case of the strong exchange interaction system above the ordering temperature. Thus the antiferromagnetism in the intermediate range of $x = 0.2-0.7$ is considered to be in short-range ordering.

3.3. Occupation of the doped holes at $x > 1.0$ and the metallic transition

For $x = 0-1.0$, as described in subsections 3.1 and 3.2, the doped holes occupy the Ni $3d_{z^2}$ orbital and $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ at $x = 1.0$ is in the LOAF state associated with the Ni^{3+} ($S = \frac{1}{2}$) spins. On further substitution of Sr above $x \sim 1.0$, there is no way to occupy primarily any orbital other than the Ni $3d_{x^2-y^2}$, because the Ni $3d_{z^2}$ orbital is empty. Here following two cases are possible: (i) the doped hole localizes on the $3d_{x^2-y^2}$ orbital and the Ni^{3+} ion undergoes a transition to the Ni^{4+} ($S = 0$) ion; (ii) the doped hole occupies the O $2p_{x,y}$ orbital in the Ni-O plane, which is hybridized strongly with the $3d_{x^2-y^2}$ orbital.

In the former case, as the number of Ni^{4+} ($S = 0$) increases linearly with increasing x above $x = 1.0$, the transition from the insulating LOAF state to the PM state must be a slow and monotonic one.

In the latter case, on the other hand, the hole spin ($S = \frac{1}{2}$) in the $2p_{x,y}$ orbital orientates antiparallel with the neighbouring Ni spin ($S = \frac{1}{2}$), giving rise to spin frustrations. This destroys the AF order of Ni^{3+} ($S = \frac{1}{2}$) spins at a low hole doping of $x - 1$ as in the case of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [21].

Above $x = 1.0$, as shown in the inset of figure 5, the ^{139}La NMR intensity observed at 1.7 K increases and quickly saturates with small Sr substitution. As x goes through $x \sim 1.0$, the $T_1^{-1} \propto T^{-2.7}$ (for $x = 0.9$) dependence of ^{139}La NMR, characteristic of the nuclear relaxation behaviour in the 3D LOAF state, changes drastically to the Korringa-like relation $T_1^{-1} \propto T$ as shown in figure 4. These results indicate that the AF order of Ni^{3+} ($S = \frac{1}{2}$) spins at $x \lesssim 1.0$ is destroyed suddenly and goes into the PM state for $x \geq 1.0$. Thus we may conclude that, for $x \gtrsim 1.0$, the doped holes occupy mainly the O $2p_{x,y}$ orbital in the Ni-O plane and the phase transition at $x \sim 1.0$ is caused by the spin frustration of the Ni^{3+} ($S = \frac{1}{2}$) spins.

Two characteristic behaviours in the Korringa-like relaxation of ^{139}La are observed in the metallic state: (i) $(T_1 T)^{-1}$ increases with decreasing x close to $x = 1.0$, similar to the x

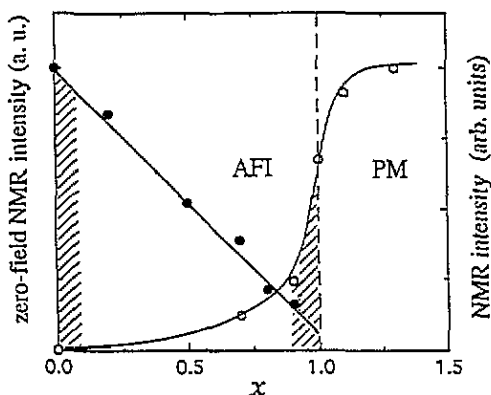


Figure 9. A phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ at low temperature. ● and ○ show the intensities of ^{139}La zero-field NMR and NMR under the external field, respectively. Solid lines are drawn as eye guides. The hatched areas located at $x \sim 0$ and at $x \sim 1.0$ indicate the LOAF associated with $S = 1$ (Ni^{2+}) and $S = \frac{1}{2}$ (Ni^{3+}) spins, respectively.

dependence of $(T_1 T)^{-1}$ observed in the metallic state of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [22] and (ii) $(T_1 T)^{-1}$ increases on lowering the external magnetic field strength. Contribution from the thermal fluctuation of a few residual Ni^{2+} ($S = 1$) ions can be ruled out because the experimental T_1 values follow the Korringa-like relation, $T_1 T = \text{constant}$, at both $H = 9.9$ kOe and $H = 36.5$ kOe. Thus these $(T_1 T)^{-1}$ enhancements are considered to relate closely to spin fluctuations of the Ni^{3+} spins associated with the 2D AF correlation.

Finally, in figure 9, we show the phase diagram of $\text{La}_{2-x}\text{Sr}_x\text{NiO}_4$ at low temperatures confirmed by the present NMR study. The solid line shows the x dependence of ^{139}La zero-field NMR intensity, which corresponds to the number of Ni^{2+} ions. The solid curve shows the dependence of the ^{139}La NMR intensity on x . The phase transition from the AF insulator to the PM occurs at $x \sim 1.0$. Two hatched areas locating close to $x \sim 0$ and ~ 1.0 indicate the long-range AF ordered state associated with $S = 1$ (Ni^{2+}) spins and with $S = \frac{1}{2}$ (Ni^{3+}) spins, respectively, where T_1^{-1} of ^{139}La is proportional to T^{-3} . In the intermediate region between the hatched areas, the system is in the short-range AF ordered state.

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