

Orbital properties of $\text{Sr}_3\text{Ru}_2\text{O}_7$ and related ruthenates probed by ^{17}O NMR

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We report a site-separated ^{17}O NMR study of the layered perovskite ruthenate $\text{Sr}_3\text{Ru}_2\text{O}_7$, which exhibits nearly two-dimensional transport properties and itinerant metamagnetism at low temperatures. The local hole occupancies and the spin densities in the oxygen $2p$ orbitals are obtained by means of tight-binding analyses of electric field gradients and anisotropic Knight shifts. These quantities are compared with two other layered perovskite ruthenates: the two-dimensional paramagnet Sr_2RuO_4 and the three-dimensional ferromagnet SrRuO_3 . The hole occupancies at the oxygen sites are very large, about one hole per ruthenium atom. This is due to the strong covalent character of the Ru-O bonding in this compound. The magnitude of the hole occupancy might be related to the rotation or tilt of the RuO_6 octahedra. The spin densities at the oxygen sites are also large, 20%–40% of the bulk susceptibilities, but in contrast to the hole occupancies, the spin densities strongly depend on the dimensionality. This result suggests that the density of states at the oxygen sites plays an essential role for the understanding of the complex magnetism found in the layered perovskite ruthenates.

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I. INTRODUCTION

The Ruddlesden-Popper (RP) series of layered perovskite ruthenates has attracted great interest because of their wide variety of phenomena. The strontium ruthenates $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ are metallic members of the RP perovskite ruthenates featuring various kinds of itinerant magnetism and magnetic fluctuations. The two-dimensional member ($n=1$) Sr_2RuO_4 is paramagnetic and exhibits unconventional superconductivity attributable to p -wave pairing,^{1–3} originating from electron correlations in the Ru $4d_{xy}$ band. At the same time, it possesses strong incommensurate antiferromagnetic fluctuations⁴ due to nesting of the $4d_{yz,zx}$ bands. The three-dimensional end member ($n=\infty$) SrRuO_3 is an itinerant ferromagnet with a Curie temperature of 160 K.⁵

The intermediate dimensional, bilayer member ($n=2$) $\text{Sr}_3\text{Ru}_2\text{O}_7$ does not exhibit magnetic order at zero magnetic field and ambient pressure. Nevertheless, $\text{Sr}_3\text{Ru}_2\text{O}_7$ is considered to be very close to a ferromagnetic instability: (a) the uniform susceptibility has a peak around 16 K, (b) the Wilson ratio is quite large ~ 10 , and (c) along c axis applying small uniaxial pressure of about 0.1 GPa pushes $\text{Sr}_3\text{Ru}_2\text{O}_7$ into a ferromagnetic phase below 80 K.^{6,7} At ambient pressure, field-induced metamagnetic transitions are observed.^{8,9} The investigation of those metamagnetic transitions leads to a phase diagram with a line of first-order phase transitions terminating at a critical end point. Furthermore, the critical end temperature T^* is extremely low, $T^*=1.2$ K for $H \perp c$, and T^* vanishes for $H \parallel c$.¹⁰ In the latter case ($H \parallel c$), the existence of a metamagnetic quantum critical point (MMQCP) was proposed.^{11,12} In our previous ^{17}O NMR study with $H \parallel c$, we reported the measurement of the nuclear spin-lattice relaxation rate $1/T_1$, which probes the spin fluctuations, and concluded that two-dimensional ferromagnetic character is dominant at high temperatures. In contrast, nonferromagnetic (mostly incommensurate antiferromagnetic) fluctuations dominate for $T \rightarrow 0$ K near the MMQCP.¹³

Such competitions between itinerant ferromagnetism and incommensurate antiferromagnetism in $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ are a result of the existence of narrow bands and a high density of states (DOS) at the Fermi level E_F created by ruthenium $4d$ and oxygen $2p$ orbitals. According to a band-structure calculation for Sr_2RuO_4 ,¹⁴ $4d$ - $2p$ antibonding bands at the Fermi level create 18% of the DOS in the oxygen $2p$ orbitals and possibly play a crucial role for the electronic and/or structural instabilities. The large DOS at the oxygen sites is unlikely for $3d$ transition-metal oxides because the covalency between the d and $2p$ orbitals is usually rather weak. Our concerns are the following: (i) how does the hole occupancy or DOS in the oxygen $2p$ orbitals affect the occurrence of itinerant ferromagnetism or antiferromagnetism and (ii) what is the relationship between dimensionality and magnetism.

In this article, we report a detailed site-separated ^{17}O NMR study of $\text{Sr}_3\text{Ru}_2\text{O}_7$. In Sec. III B, we estimate the hole occupancies in the $2p$ orbitals from the NMR quadrupole splittings at the oxygen sites. Since the oxygen $2p$ orbitals feature a magnetic-dipole type of hyperfine interaction, the anisotropy of the Knight shifts needs to be considered. In Sec. III C we obtain the spin susceptibility of each orbital at all oxygen sites from the Knight shifts. For comparison, we also analyze the related ruthenates Sr_2RuO_4 and SrRuO_3 applying the same method.

II. EXPERIMENT

In our NMR experiment we used single crystals of $\text{Sr}_3\text{Ru}_2\text{O}_7$ which were grown in a floating-zone image furnace.¹⁵ We exchanged natural oxygen ^{16}O ($I=0$) for ^{17}O ($I=5/2$). The substitution was performed in a silica-glass-tube furnace, where the samples were kept for one week at 1050 °C in a 70%-concentrated $^{17}\text{O}_2$ atmosphere. Although the gain of mass, estimated to be 0.9%, could not be observed, the measured ^{17}O NMR signals assure that the iso-

tope substitution process was successful at least over the penetration depth accessible in our experiment—i.e., several micrometers. This is sufficient to ignore surface-related effects. After the annealing process, we confirmed the residual in-plane resistivity to be $0.8 \mu\Omega \text{ cm}$. This is clean enough to observe the intrinsic behavior of this system.¹⁶

Great care was taken to keep the orientation of the sample throughout the field-dependent measurements. For this purpose, complex rf components were introduced outside the cryostat. This ensured that the measurements for all desired field strengths, corresponding to frequencies of 10–80 MHz, could be carried out using only one probing coil. A homemade wideband preamplifier designed with high-electron-mobility transistors was immersed in liquid nitrogen to obtain an excellent noise figure of 0.5 dB. Furthermore, it had a short dead time of less than $3 \mu\text{s}$ after saturation. With this setup it was possible to overcome the issues of the weak intensities of signals and shortness of NMR decoherence times.

III. RESULTS AND DISCUSSIONS

A. NMR spectra and site assignment

^{17}O NMR lines can be described using anisotropic Knight shifts and the quadrupole interaction perturbation of the electric field gradients (EFGs). For each site, the resonance field H_{res} corresponding to the $m \leftrightarrow m-1$ resonance can be approximately written as,^{19,42}

$$\frac{H_0 - H_{\text{res}}}{H_{\text{res}}} = {}^{17}K^{\text{iso}} + \left\{ \frac{1}{2} \frac{{}^{17}\nu_{\text{Q}} \left(m - \frac{1}{2} \right)}{{}^{17}\gamma H_{\text{res}}} + \frac{1}{2} {}^{17}K^{\text{ax}} \right\} \times (3 \cos^2 \theta - 1) - \frac{1}{2} \left\{ {}^{17}K^{\text{aniso}, \perp} + \left(m - \frac{1}{2} \right) \frac{{}^{17}\nu_{\text{Q}}}{{}^{17}\gamma H_{\text{res}}} \eta \right\} \sin^2 \theta \cos 2\phi, \quad (1)$$

where (θ, ϕ) are Euler's coordinates with respect to the largest principal axis of the diagonalized EFG and ${}^{17}\gamma$ ($=5.7719 \text{ MHz/T}$) is the gyromagnetic ratio of an ^{17}O nucleus. H_0 is the resonance field of a free ^{17}O atom at the resonance frequency ${}^{17}\gamma H_0$. ${}^{17}K^{\text{iso}}$ is the isotropic Knight shift, ${}^{17}K^{\text{ax}}$ is the axial anisotropic shift, and ${}^{17}K^{\text{aniso}, \perp}$ is the in-plane anisotropic shift perpendicular to the principal axis for lower symmetric sites. ${}^{17}\nu_{\text{Q}}$ is the pure quadrupole frequency, and η ($0 \leq \eta \leq 1$) is the asymmetric parameter of the EFG.

Crystallographically, three inequivalent oxygen sites exist in the bilayered perovskite structure (Fig. 1). Moreover, when a field is applied perpendicular to the c axis, the in-plane site O(3) splits into two configurations $\text{O}(3)^{\parallel}$ and $\text{O}(3)^{\perp}$, as shown in Fig. 2(a). Figure 3 shows a typical ^{17}O NMR spectra for $\text{Sr}_3\text{Ru}_2\text{O}_7$.

For the apical sites [O(1) and O(2) in $\text{Sr}_3\text{Ru}_2\text{O}_7$] one can rewrite the parameters as follows:

$${}^{17}K^{\text{iso}} = \frac{1}{3} ({}^{17}K_{\text{obs}}^c + 2{}^{17}K_{\text{obs}}^{a,b}),$$

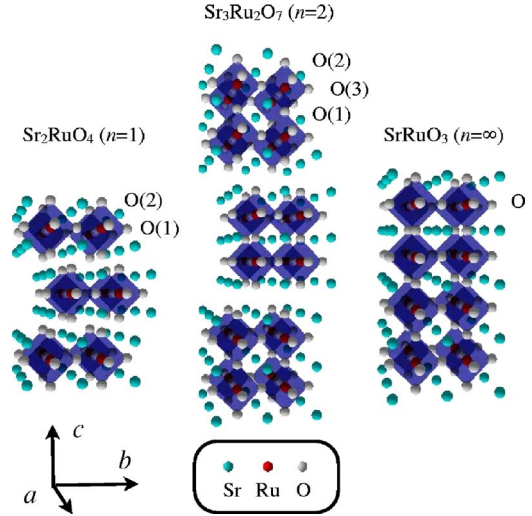


FIG. 1. (Color online) Crystal structure of the Ruddlesden-Popper series $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ for Sr_2RuO_4 ($n=1$, left), $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n=2$, middle), and SrRuO_3 ($n=\infty$, right). The axes a and b are taken along a Ru-O-Ru bonding. For $\text{Sr}_3\text{Ru}_2\text{O}_7$ and SrRuO_3 , symmetries are reduced because of a rotation and a tilt of the RuO_6 octahedra, respectively (Refs. 17 and 18). For simplicity, these effects are not shown. There are apical O(2) and in-plane O(1) sites in Sr_2RuO_4 . $\text{Sr}_3\text{Ru}_2\text{O}_7$ has two kinds of apical sites. For $\text{Sr}_3\text{Ru}_2\text{O}_7$, we label the inner-apical, outer-apical, and in-plane sites O(1), O(2), and O(3) sites, respectively.

$$\begin{aligned} {}^{17}K^{\text{ax}} &= {}^{17}K_{\text{obs}}^c - {}^{17}K^{\text{iso}} = \frac{2}{3} ({}^{17}K_{\text{obs}}^c - {}^{17}K_{\text{obs}}^{a,b}), \\ {}^{17}K^{\text{aniso}, \perp} &= 0, \\ {}^{17}\nu_{\text{Q}} &= {}^{17}\nu^c = -2{}^{17}\nu^{a,b}, \\ \eta &= 0. \end{aligned}$$

Here, ${}^{17}K_{\text{obs}}^i$ is the observed Knight shift for direction i .

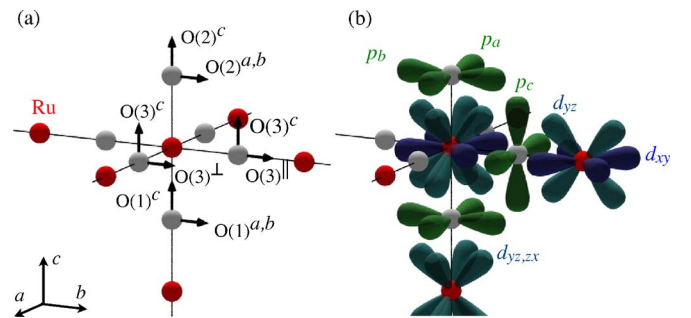


FIG. 2. (Color online) (a) ^{17}O NMR spectral site notations for $\text{Sr}_3\text{Ru}_2\text{O}_7$. Arrows denote the corresponding field directions $H \parallel c$ and $H \parallel [100]$. (b) Relevant atomic orbitals at the Fermi surfaces for $\text{Sr}_3\text{Ru}_2\text{O}_7$. We treat interactions of electrons with nuclei by a method of linear combination of atomic orbitals: namely, the tight-binding method. Ru^{4+} ions realize a low-spin configuration, and the resulting t_{2g} ($=4d_{xy}, 4d_{yz}, 4d_{zx}$) orbitals hybridize with the oxygen $2p_{\pi}$ ($=2p_x, 2p_y, 2p_z$) orbitals.

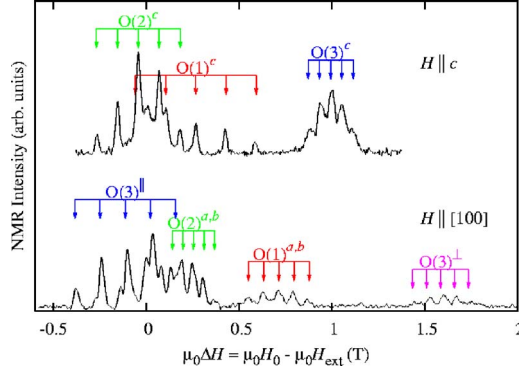


FIG. 3. (Color online) Field-swept ^{17}O -NMR spectra for $\text{Sr}_3\text{Ru}_2\text{O}_7$ with a frequency of 72.5 MHz at 1.7 K. The corresponding ^{17}O NMR field for a free atom, $\mu_0 H_0$, is 12.56 T. H_{ext} is the external applied field. Lines from each site must consist of five resonances due to the perturbations from the electric quadrupole interaction. The unassigned sites, which exhibit a smaller sample-dependent intensity, are attributed to an impurity phase of Sr_2RuO_4 .

For in-plane sites [O(3) for $\text{Sr}_3\text{Ru}_2\text{O}_7$] the parameters are

$$^{17}K^{\text{iso}} = \frac{1}{3}(^{17}K_{\text{obs}}^{\parallel} + ^{17}K_{\text{obs}}^{\perp} + ^{17}K_{\text{obs}}^c),$$

$$^{17}K^{\text{ax}} = ^{17}K_{\text{obs}}^{\parallel} - ^{17}K^{\text{iso}},$$

$$^{17}K^{\text{aniso},\perp} = ^{17}K_{\text{obs}}^{\perp} - ^{17}K_{\text{obs}}^c,$$

$$^{17}\nu_{\text{Q}} = ^{17}\nu^{\parallel}.$$

From Eq. (1), we expect a linear relationship between $(H_0 - H_{\text{res}})/H_{\text{res}}$ and $(H_{\text{res}})^{-1}$ as long as the magnetization M is linear with H . Figure 4 displays such a behavior for $H \parallel [100]$ (see Ref. 20 for $H \parallel c$). The linear relationships are realized much below and above the metamagnetic field H_M .

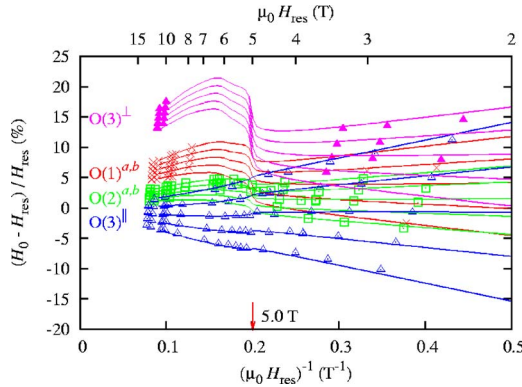


FIG. 4. (Color online) NMR spectral positions as a function of H_{res}^{-1} for $\text{Sr}_3\text{Ru}_2\text{O}_7$ with $H \parallel [100]$. All data points are taken from the field-swept spectra at 1.7 K. The arrow denotes the metamagnetic field. At and slightly below the metamagnetic field high transverse relaxation rates $1/T_2$ prevent observations of signals from the O(1) and O(3) $^{\perp}$ sites. The plotted lines are based on Eq. (1). The values of EFGs are listed in Sec. III B. The Knight shifts are evaluated in Sec. III C.

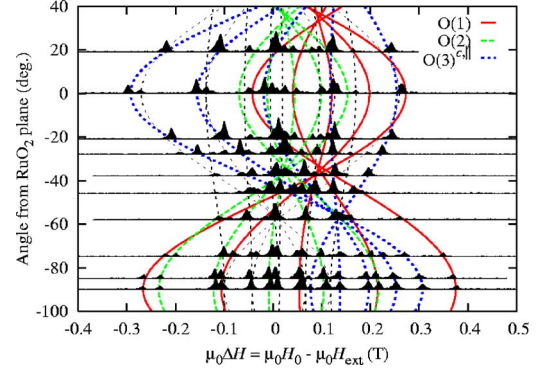


FIG. 5. (Color online) Field-swept NMR spectra with various field orientations for $\text{Sr}_3\text{Ru}_2\text{O}_7$ at 1.7 K with a frequency of 21.3 MHz— i.e., $\mu_0 H_0 \sim 3.7$ T. The orientation is varied from [100] (0° in the plot) to the c axis ($\pm 90^\circ$) by the use of a backlash-free rotator in an 8-T split-coil magnet. All curves are drawn in the same scheme as in Fig. 4. The O(3) $^{\perp}$ lines are not observable in this configuration due to a high transverse relaxation rate $1/T_2$. The narrow dotted curves, which are not attributable to $\text{Sr}_3\text{Ru}_2\text{O}_7$, originate from the Sr_2RuO_4 -O(1) site in the impurity phase.

The plot is helpful to group spectral lines split up by EFG into identical sites. Applying different field orientations causes different responses of the apical and in-plane sites (Fig. 5). In this way one can distinguish between them. The difference between the inner-apical O(1) and outer-apical O(2) sites appears in the spectral intensities as the corresponding composition ratio 1:2, as long as the spectrum is taken under the condition that the relaxation effects be small. Thus, the three sites in $\text{Sr}_3\text{Ru}_2\text{O}_7$ can be resolved from the complicated spectra shown in Fig. 3.

As displayed in Figs. 3 and 5, the impurity eutectic phase of Sr_2RuO_4 sometimes appears in NMR spectra, although the fraction of Sr_2RuO_4 in the powder x-ray diffraction spectra of our samples does not exceed a few percent. This is possible if during the annealing process the substitution of the oxygen atoms in the minor Sr_2RuO_4 part for ^{17}O is easier than the substitution in the $\text{Sr}_3\text{Ru}_2\text{O}_7$ part of the sample. The spectra positions and longitudinal relaxation rates $1/T_1$ of Sr_2RuO_4 are known,²¹ and hence, line crossing between $\text{Sr}_3\text{Ru}_2\text{O}_7$ and Sr_2RuO_4 can be avoided when measuring Knight shifts or $1/T_1$ of $\text{Sr}_3\text{Ru}_2\text{O}_7$.

B. Quadrupole splitting

The EFG at the oxygen site is the sum of the fields created by external ions and by on-site unclosed $2p$ shells. The former is largely enhanced over the value obtained by point-charge calculations due to polarization of the on-site closed shells. We employ the Sternheimer equation^{22,23} to describe the EFG frequencies $^{17}\nu^j$:

$$^{17}\nu^j = (1 - \gamma_{\infty})^{17}\nu_{\text{lat}}^j + (1 - R)^{17}\nu_{\text{hole}}^j, \quad (2)$$

where $^{17}\nu_{\text{lat}}^j$ is obtained from the EFG frequency of the point-charge calculation and $^{17}\nu_{\text{hole}}^j$ is that of the holes in the $2p$ orbitals. The two Sternheimer parameters γ_{∞} and R are the antishielding and shielding factors, respectively. R is ap-

TABLE I. Electric field gradients' (EFG) frequencies of the ruthenates determined from the observed electric quadrupole splittings, compared with those obtained from point-charge model calculations where the charges of the oxygen and the ruthenium are -2 and $+4$, respectively. The signs have been adjusted to obtain positive EFG frequencies along the principal axes. Order-of-magnitude differences between experimentally determined EFG's and calculated EFG's mostly arise from an antishielding effect $(1 - \gamma_\infty)$. Lattice parameters used for the calculations are based on Refs. 17, 27, and 18, for $\text{Sr}_3\text{Ru}_2\text{O}_7$, Sr_2RuO_4 , and SrRuO_3 , respectively.

	$^{17}\nu_{\parallel}^{a}$ (MHz)	$^{17}\nu_{\perp}^{b}$ (MHz)	$^{17}\nu^c$ (MHz)	η	$^{17}\nu_{\text{lat}}^{a}$ (MHz)	$^{17}\nu_{\text{lat}}^{\perp,b}$ (MHz)	$^{17}\nu_{\text{lat}}^c$ (MHz)	η_{lat}
$\text{Sr}_3\text{Ru}_2\text{O}_7$								
O(1)	∓ 0.47	∓ 0.47	± 0.94	0	-0.0830	-0.0830	0.1660	0
O(2)	∓ 0.33	∓ 0.33	± 0.66	0	-0.0456	-0.0456	0.0910	0
O(3)	± 0.78	∓ 0.44	∓ 0.34	0.11	0.1951	-0.0971	-0.0980	0.004
Sr_2RuO_4								
O(1)	$\pm 0.77^a$	$\mp 0.45^a$	$\mp 0.32^a$	0.17^a	0.2062	-0.0986	-0.1064	0.04
O(2)	$\mp 0.305^a$	$\mp 0.305^a$	$\pm 0.610^a$	0^a	-0.0437	-0.0437	0.0874	0
Paramagnetic SrRuO_3								
O	$\pm 0.95^b$				0.1782	-0.0891	-0.0891	0

^aH. Murakawa *et al.*, single crystal with an accurate sample alignment in Ref. 28. Values are the same in Ref. 21 within errors.

^bK. Yoshimura *et al.*, powder sample in Ref. 29.

proximately 0.1 for oxygen $2p$,^{22,23} and we adopt this value. It is difficult to estimate the value of γ_∞ for O^{2-} . ^{17}O NMR experiments in cuprates yielded γ_∞ of -8 (Ref. 24) or -9 (Ref. 25). However, theoretical calculations suggested a wide variety of values between -9 and -33 ,²⁶ indicating that the value is highly dependent on the ionic radius or covalency.²³

Table I shows the measured EFG frequencies $^{17}\nu^i$ determined from the quadrupole splitting of the satellite lines and $^{17}\nu_{\text{lat}}^i$ from calculations based on the point-charge model without considering holes at the oxygen sites. In the calculation, ions within at least three lattice units have to be included to obtain sufficient convergence. The spectral EFG frequencies do not feature any significant H and T (< 100 K) dependence, suggesting that the electronic band structure of $\text{Sr}_3\text{Ru}_2\text{O}_7$ is not strongly modified by the first-order metamagnetic transition. In fact, de Haas-van Alphen³⁰ and Shubnikov-de Haas¹⁶ measurements revealed that the changes in the oscillating frequencies are quite small, supporting a field-induced Stoner transition model of the itinerant metamagnetism of $\text{Sr}_3\text{Ru}_2\text{O}_7$.

In the metallic ruthenate, the Fermi level is located between the bonding and antibonding molecular orbitals,¹⁴ and hence, the atomic $2p$ orbitals acquire holes. In terms of the hole occupancy h_{2p} of the $2p$ orbital, the induced EFG $^{17}\nu_{\text{hole}}^i$ can be written as

$$\begin{pmatrix} ^{17}\nu_{\text{hole}}^x \\ ^{17}\nu_{\text{hole}}^y \\ ^{17}\nu_{\text{hole}}^z \end{pmatrix} = \frac{2}{5} e h_{2p} \langle r^{-3} \rangle_{2p} \begin{pmatrix} -1 \\ -1 \\ 2 \end{pmatrix}, \quad (3)$$

for the $2p_z$ orbital, for instance. Taking $\langle r^{-3} \rangle_{2p}$ to be 3.63 a.u., which is a 70% value of that for a free atom,^{25,35} $^{17}\nu_{\text{hole}}^i = h_{2p}(-1.33, -1.33, 2.66)$ MHz. Thus, the total EFG frequency at each site is, for the apical sites,

$$\begin{pmatrix} ^{17}\nu^{a,b} \\ ^{17}\nu^c \end{pmatrix} = (1 - \gamma_\infty) ^{17}\nu_{\text{lat}}^i + (1 - R) h_{2p_{a,b}} \begin{pmatrix} 1.33 \text{ MHz} \\ -2.66 \text{ MHz} \end{pmatrix} \quad (4)$$

or, for the in-plane sites,

$$\begin{pmatrix} ^{17}\nu_{\parallel} \\ ^{17}\nu_{\perp} \\ ^{17}\nu^c \end{pmatrix} = (1 - \gamma_\infty) ^{17}\nu_{\text{lat}}^i + (1 - R) h_{2p_c} \begin{pmatrix} -1.33 \text{ MHz} \\ -1.33 \text{ MHz} \\ 2.66 \text{ MHz} \end{pmatrix} + (1 - R) h_{2p_{a,b}} \begin{pmatrix} -1.33 \text{ MHz} \\ 2.66 \text{ MHz} \\ -1.33 \text{ MHz} \end{pmatrix}. \quad (5)$$

The antishielding factor γ_∞ cannot be solved from the above equations because of the dipole-field requirement $\sum_i ^{17}\nu^i = 0$. Table II shows the hole occupancy in each orbital estimated from various values for γ_∞ and from band-structure calculations in the literature. In this analysis, $\gamma_\infty < -8$ is necessary to make all densities positive. In the following we adopt the same value used in the case of the cuprates $\gamma_\infty = -9$.^{23,25} This leads to a physically reasonable set of values for h_{2p} .

It should be noted that most of the holes reside at the in-plane sites [O(3) for $\text{Sr}_3\text{Ru}_2\text{O}_7$ and O(1) for Sr_2RuO_4], reflecting their quasi-two-dimensionality. The large magnitude of the in-plane hole occupancy is in agreement with the strongly anisotropic conductivity [$\rho_c/\rho_{ab} \approx 300$ for $\text{Sr}_3\text{Ru}_2\text{O}_7$ (Ref. 6) and ≥ 400 for Sr_2RuO_4 (Ref. 2)] and with spin den-

TABLE II. Hole occupancies in the oxygen 2*p* orbitals obtained from the EFG analysis. Although the derivation of a reliable value of the Sternheimer antishielding factor γ_∞ is technically difficult, we argue that $\gamma_\infty = -9$ yields physically reasonable results (see text). h_{2p}^{total} denotes the total hole number per ruthenium atom. The given literature values of band-structure calculations have been estimated by integrating the DOS above E_F .

	NMR EFG analysis			Band calc.
	γ_∞			
	-8	-9	-10	
	Sr ₃ Ru ₂ O ₇			
$h_{2p_{a,b}}^{\text{O}(1)}$	0.056	0.075	0.092	
$h_{2p_{a,b}}^{\text{O}(2)}$	0.005	0.009	0.021	
$h_{2p_{a,b}}^{\text{O}(3)}$	0.178	0.199	0.218	
$h_{2p_c}^{\text{O}(3)}$	0.232	0.256	0.277	
$h_{2p}^{\text{O}(3)}$	0.410	0.455	0.495	0.28 ^a
h_{2p}^{total}	0.866	1.00	1.12	0.76 ^a
	Sr ₂ RuO ₄			
$h_{2p_{a,b}}^{\text{O}(1)}$	0.183	0.202	0.219	
$h_{2p_c}^{\text{O}(1)}$	0.276	0.301	0.323	
$h_{2p}^{\text{O}(1)}$	0.459	0.503	0.542	0.27 ^b 0.28 ^c
$h_{2p_{a,b}}^{\text{O}(2)}$	-0.001	0.012	0.023	
$h_{2p}^{\text{O}(2)}$	-0.002	0.024	0.046	0.15 ^b 0.09 ^c
h_{2p}^{total}	0.915	1.05	1.18	0.84 ^b 0.75 ^c
	Paramagnetic SrRuO ₃			
h_{2p}^{O}	0.120	0.143	0.164	
h_{2p}^{total}	0.718	0.859	0.984	

^aAfter Fig. 4 in Ref. 31.

^bAfter Fig. 3 in Ref. 14.

^cAfter Fig. 4 in Ref. 32.

sities derived from the Knight shift measurements, which are discussed later.

Another remark concerns the relationship between hole occupancy and bonding covalency. In general, a hole in an antibonding molecular orbital introduces covalent character in the original ionic bond. Since a covalent bonding is sensitive to the Ru-O-Ru angle, the covalency can be related to a structural instability of the RuO₆ octahedra. In Sr₂RuO₄, Oguchi argued that the high h_{2p_c} in the $4d_{z_x, y_z} - 2p_c$ (one of

p_π) antibonding orbitals may account for an absence of a rotation of the RuO₆ octahedra.¹⁴ Indeed, in Table II, h_{2p_c} , which is hybridized with d_{z_x, y_z} , has a larger value (=0.301) than $h_{2p_{a,b}}$ (=0.202) hybridizing with d_{xy} at the in-plane sites. In addition, a smaller value of h_{2p_c} (=0.256) at the in-plane site is obtained for Sr₃Ru₂O₇, where the RuO₆ octahedra are rotated by 7°. ¹⁷ We consider that the existence of the rotation in Sr₃Ru₂O₇ is related to a weaker covalency in the $d_{z_x, y_z} - 2p_c$ bond than that in Sr₂RuO₄. For comparison with SrRuO₃, which has an octahedra tilt, the hole occupancy per ruthenium atom h_{2p}^{total} can be used. SrRuO₃ has the smallest value of h_{2p}^{total} in Table II, which means the weakest covalency per ruthenium atom. This might be related to the occurrence of the tilt in SrRuO₃ as well as the rotation in Sr₃Ru₂O₇.

We point out experimentally that the hole content of the antibonding orbitals may be substantially relevant to the distortion of the RuO₆ octahedra even in Sr_{*n*+1}Ru_{*n*}O_{3*n*+1} which have the same tolerance factor.

C. Knight shift

Generally, the observed Knight shift $^{17}\text{K}_{\text{obs}}^i$ (or the uniform susceptibility χ_{bulk}^i) for a given field direction i ($=x, y, z$) is the sum of the temperature-independent orbital part $^{17}\text{K}_{\text{orb}}^i$ ($\chi_{\text{bulk, orb}}^i$), the diamagnetic part $^{17}\text{K}_{\text{dia}}^i$ ($\chi_{\text{bulk, dia}}^i$), and the temperature-dependent spin part $^{17}\text{K}_{\text{s}}^i$ ($\chi_{\text{bulk, s}}^i$), which are expressed as follows:

$$^{17}\text{K}_{\text{obs}}^i(T) = ^{17}\text{K}_{\text{orb}}^i + ^{17}\text{K}_{\text{dia}}^i + ^{17}\text{K}_{\text{s}}^i(T), \quad (6)$$

$$\chi_{\text{bulk}}^i(T) = \chi_{\text{bulk, orb}}^i + \chi_{\text{bulk, dia}}^i + \chi_{\text{bulk, s}}^i(T), \quad (7)$$

$$^{17}\text{K}_{\text{s}}^i(T) = \frac{^{17}A_{\text{s}}^i}{N_{\text{A}}\mu_{\text{B}}} \chi_{\text{s}}^i(T). \quad (8)$$

Here, N_{A} , μ_{B} , and $^{17}A_{\text{s}}^i$ denote Avogadro's number, the Bohr magneton, and the spin hyperfine coupling constant, respectively. Note that the spin part of M/H_{res} must be used instead of the differential susceptibility $\chi_{\text{bulk, s}}^i$ in Eq. (8) unless M is proportional to H .

Figure 6 shows a $^{17}\text{K}_{\text{obs}}^i$ vs M/H_{res} plot of Sr₃Ru₂O₇. $^{17}\text{K}_{\text{obs}}^i$ and M/H_{res} are measured at ~ 4 T by changing temperature in a range of 1.7–100 K passing through the susceptibility maximum at 16 K [Fig. 6(a)] and at 1.7 K by changing the magnetic field in a range of 3–13 T across the metamagnetic field [Fig. 6(b)]. For the [100] direction, the temperature dependence for the O(1) site could not be measured due to the crossing of the lines to other sites. Linear relations are obtained in both cases, and the solid lines are linear fits. The slopes of the K vs M/H_{res} plots for those two sets of data give the same hyperfine coupling constant $^{17}A_{\text{s}}^i$. The orbital components of the Knight shifts are negligibly small since the lines intersect the origin. The obtained spin hyperfine coupling constants $^{17}A_{\text{s}}^i$ are listed in Table III.

We extended the previous tight-binding approach³³ by including the magnetic-dipolar fields from neighboring sites:

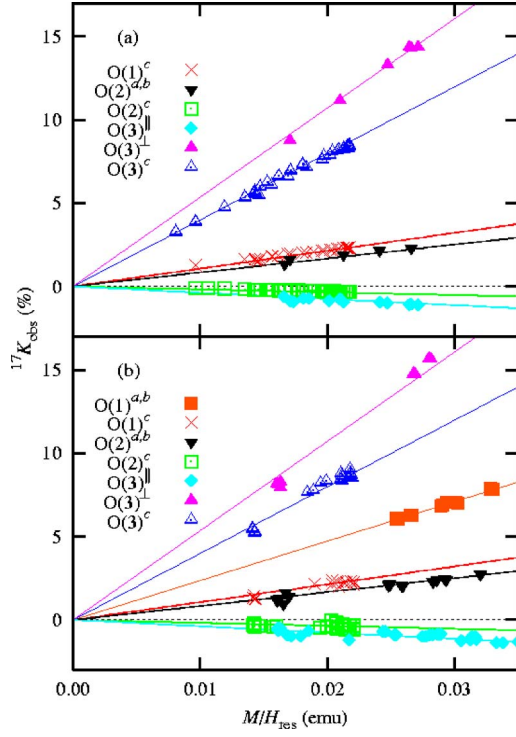


FIG. 6. (Color online) $^{17}\text{K}_{\text{obs}}$ vs M/H_{res} plots for $\text{Sr}_3\text{Ru}_2\text{O}_7$. The fitted hyperfine coupling constant for each curve is listed in Table III. (a) Temperature varied data points between 1.7 K and 100 K at low field ≈ 4 T and (b) field varied points between 3 T and 13 T at 1.7 K. Below 7 T M is measured with a commercial superconducting quantum interference device (SQUID) magnetometer. For higher fields, M is interpolated (7–8 T), derived from 2.8 K data given in Ref. 8 (8–11 T), and extrapolated (>11 T).

$$^{17}\text{K}_{\text{obs}}^i = ^{17}\text{K}_{\text{off-site}}^i + ^{17}\text{K}_{\text{on-site}}^i. \quad (9)$$

The first term denotes the shift of the field produced by the moment of the adjacent sites, mostly of the nearest-neighbor ruthenium sites, and the second term is produced by the transferred spin densities in the oxygen on-site orbitals. In our case, the latter plays a major role as a result of a large local spin density.

The off-site part at the oxygen n site is written in terms of local susceptibilities at neighboring m sites χ_m^i :

$$^{17}\text{K}_{\text{off-site,orb}}^i = \frac{1}{N_A \mu_B} \sum_{m(\neq n)} \frac{\partial^2}{\partial t^2} \left(\frac{1}{r_{mn}} \right) \chi_{m,\text{orb}}^i,$$

$$^{17}\text{K}_{\text{off-site,dia}}^i = \frac{1}{N_A \mu_B} \sum_{m(\neq n)} \frac{\partial^2}{\partial t^2} \left(\frac{1}{r_{mn}} \right) \chi_{m,\text{dia}}^i,$$

$$^{17}\text{K}_{\text{off-site,s}}^i(T) = \frac{1}{N_A \mu_B} \sum_{m(\neq n)} \frac{\partial^2}{\partial t^2} \left(\frac{1}{r_{mn}} \right) \chi_{m,s}^i(T). \quad (10)$$

Here, r_{mn} is the distance between two sites m and n . The summations are taken over a distance of four lattice units to ensure convergence. Since $\chi_{\text{bulk},s}$ of $\text{Sr}_3\text{Ru}_2\text{O}_7$ and SrRuO_3 are strongly enhanced [$>1 \times 10^{-2}$ emu/(Ru mol)], the orbital part or diamagnetic part of χ [typically

TABLE III. ^{17}O Hyperfine coupling constants $^{17}A_s$, $^{17}A_s$ of $\text{Sr}_3\text{Ru}_2\text{O}_7$ are obtained from fittings of $^{17}\text{K}_{\text{obs}}$ vs M/H_{res} plots (Fig. 6). Estimated nonspin parts of the Knight shifts $^{17}\text{K}_{\text{orb}} + ^{17}\text{K}_{\text{dia}}$ for Sr_2RuO_4 are also shown. For the other compounds, the nonspin parts are negligibly small.

	$^{17}A_s$ (kOe/ μ_B)	$^{17}\text{K}_{\text{orb}} + ^{17}\text{K}_{\text{dia}}$ (%)
$\text{Sr}_3\text{Ru}_2\text{O}_7$		
O(1) ^{a,b}	13.2 ± 0.2	
O(1)	6.0 ± 0.2	
O(2) ^{a,b}	4.7 ± 0.3	
O(2)	-0.97 ± 0.05	
O(3) ^{parallel}	-2.1 ± 0.3	
O(3) ^{perp}	29.9 ± 0.3	
O(3)	22.3 ± 0.4	
Sr_2RuO_4		
O(1) ^{parallel}	-7.9 ± 1 ^a	0.013
O(1) ^{perp}	33.1 ± 1 ^a	-0.006
O(1)	23.7 ± 1 ^a	-0.005
O(2) ^{a,b}	6.4 ± 1 ^a	-0.003
O(2)	1.9 ± 1 ^a	0.004
Paramagnetic SrRuO_3		
O ^{parallel}	6.3 ± 2 ^b	
O ^{perp}	21 ± 2 ^b	

^aH. Murakawa *et al.*, single crystal with an accurate sample alignment in Ref. 28. Knight shifts are taken below 4 K and are the same in Ref. 33 within errors.

^bAnisotropic Knight shifts are estimated from the powder patterns above T_C by pattern simulations. The spectra used in the study of Ref. 29 were provided by Yoshimura *et al.*

10^{-4} emu/(Ru mol) (Ref. 33)] for those compounds can be neglected. For Sr_2RuO_4 , the estimated values of $^{17}\text{K}_{\text{orb}} + ^{17}\text{K}_{\text{dia}}$ are also given in Table III. For all three compounds, the off-site hyperfine coupling constants from the ruthenium sites to the oxygen sites $|\sum_{m=\text{Ru}} \frac{\partial^2}{\partial t^2} \left(\frac{1}{r_{mn}} \right)|$ is small (<5 kOe/ μ_B). Therefore, the ^{17}O Knight shifts are dominated by the on-site spin parts, which we will discuss next.

Assuming that only the ruthenium orbitals contribute to the orbital part of the bulk susceptibility, the on-site Knight shifts at the oxygen sites arise solely from the spin part,

$$^{17}\text{K}_{\text{on-site}}^i(T) = \sum_{k=\{2p,a,b,c,2s\}} \frac{^{17}A_k^i}{N_A \mu_B} \chi_{k,s}^i(T), \quad (11)$$

where $^{17}A_k^i$ is the hyperfine coupling constant, $\chi_{k,s}^i(T)$ is the transferred spin density, and the subscript k ($=2p, 2s$) specifies the orbital. Since the isotropic hyperfine coupling of the $2s$ orbital $^{17}A_{2s}$ is quite large due to its Fermi contact to the nucleus [$^{17}A_{2s} \sim 3000$ kOe/ μ_B (Ref. 34)], isotropic shifts still dominate even with a tiny spin density in the $2s$ orbitals. The hyperfine couplings of $2p$ orbitals have an anisotropic dipole character $2 ^{17}A_{2p}(-1, -1, 2)$ for each $2p$ orbital, where $^{17}A_{2p} = \frac{2}{5} \mu_B \langle r^{-3} \rangle_{2p} \approx 91$ kOe/ μ_B .^{25,35}

Next, we assume that the ratios of transferred orbital spin densities, $\chi_{k,s}/\chi_{\text{bulk},s}$ ($k=2p, 2s$), are independent of the field orientation even in the case of anisotropic spin susceptibilities. Nonbonding $2p_\sigma$ orbitals can be ignored because states arising from those orbitals are much below E_F . Thus, the total on-site hyperfine coupling constant $^{17}A_{s,\text{on-site}}$ for each field orientation is simplified to, for the apical sites,

$$\begin{pmatrix} ^{17}A_{s,\text{on-site}}^{a,b} \\ ^{17}A_{s,\text{on-site}}^c \end{pmatrix} = \begin{pmatrix} 1 & 1 \\ -2 & 1 \end{pmatrix} \begin{pmatrix} 2^{17}A_{2p}\chi_{2p,x,y,s}/\chi_{\text{bulk},s} \\ ^{17}A_{2s}\chi_{2s,s}/\chi_{\text{bulk},s} \end{pmatrix} \quad (12)$$

or, for the in-plane sites,

$$\begin{pmatrix} ^{17}A_{s,\text{on-site}}^{\parallel} \\ ^{17}A_{s,\text{on-site}}^{\perp} \\ ^{17}A_{s,\text{on-site}}^c \end{pmatrix} = \begin{pmatrix} -1 & -1 & 1 \\ 2 & -1 & 1 \\ -1 & 2 & 1 \end{pmatrix} \begin{pmatrix} 2^{17}A_{2p}\chi_{2p,x,y,s}/\chi_{\text{bulk},s} \\ 2^{17}A_{2p}\chi_{2p,c,s}/\chi_{\text{bulk},s} \\ ^{17}A_{2s}\chi_{2s,s}/\chi_{\text{bulk},s} \end{pmatrix} \quad (13)$$

Since the spin density at strontium sites can be ignored, the bulk spin susceptibility $\chi_{\text{bulk},s}$ is the sum of the spin densities in the oxygen and the ruthenium orbitals,

$$\chi_{\text{bulk},s} = \chi_s^{\text{Ru}} + \chi_{2p,s}^{\text{total}} + \chi_{2s,s}^{\text{total}}. \quad (14)$$

For Sr₃Ru₂O₇, the total spin densities over all oxygen sites per ruthenium atom, $\chi_{2p,s}^{\text{total}}$ and $\chi_{2s,s}^{\text{total}}$, are

$$\chi_{2p,s}^{\text{total}} = \chi_{2p,a,b,s}^{\text{O}(1)} + 2\chi_{2p,a,b,s}^{\text{O}(2)} + 2\chi_{2p,a,b,s}^{\text{O}(3)} + 2\chi_{2p,c,s}^{\text{O}(3)}, \quad (15)$$

$$\chi_{2s,s}^{\text{total}} = \frac{1}{2}\chi_{2s,s}^{\text{O}(1)} + \chi_{2s,s}^{\text{O}(2)} + 2\chi_{2s,s}^{\text{O}(3)}. \quad (16)$$

Thus, the observed anisotropic Knight shifts can be decomposed into the local spin density in each orbital from Eqs. (6)–(16).

Table IV displays the local spin densities in the oxygen orbitals obtained from Knight shifts and the DOS at E_F , $D(E_F)$ from band-structure calculations in the literature. The spin density is generally enhanced over the value of $D(E_F)$ which comes out of band-structure calculations due to Stoner enhancement and untreated electron-electron correlations. The bulk susceptibility of Sr₃Ru₂O₇ is the product of the value inferred from the electronic specific heat and the large Wilson ratio 10 (Ref. 6). If such a Stoner enhancement varies between bands and/or site by site, the enhancement factors applied to local spin densities would differ from orbital to orbital. In Table IV, the normalized values of spin densities and of $D(E_F)$ are essentially comparable for each oxygen site. The Stoner enhancement of these ruthenates appears to be independent of the orbitals.

According to this analysis, the total spin density at the oxygen sites amounts to 20%–40% of the bulk susceptibility. This is quite large for a metallic oxide. Indeed, a polarized neutron scattering study of the exchange-enhanced paramagnet Ca_{1.5}Sr_{0.5}RuO₄ by Gukasov and co-workers⁴⁰ revealed that the in-plane site O(1) and apical sites O(2) have 30% and 4% of the total moment, respectively, and a total of one-third of moments reside at the oxygen sites. In the case of Sr₂RuO₄ the values are similar to our results shown in Table IV.

TABLE IV. Orbital spin densities obtained from Knight-shift measurements and the density of states at the Fermi level $D(E_F)$ at the oxygen site extracted from the results of band-structure calculations. Spin densities and $D(E_F)$ are normalized by the bulk spin susceptibility per ruthenium atom $\chi_{\text{bulk},s}$.

	$\chi(\text{per orb})/\chi_{\text{bulk},s}$ (%)	$\chi(\text{per Ru})/\chi_{\text{bulk},s}$ (%)	$D(E_F)$ (%)
Sr ₃ Ru ₂ O ₇			
$\chi_{2p,a,b,s}^{\text{O}(1)}$	1.71±0.06	1.71±0.06	3 ^a
$\chi_{2s,s}^{\text{O}(1)}$	0.360±0.005	0.180±0.003	
$\chi_{2p,a,b,s}^{\text{O}(2)}$	1.50±0.06	3.00±0.11	2 ^a
$\chi_{2s,s}^{\text{O}(2)}$	0.093±0.007	0.093±0.007	
$\chi_{2p,a,b,s}^{\text{O}(3)}$	6.38±0.08	12.8±0.16	
$\chi_{2p,c,s}^{\text{O}(3)}$	5.03±0.09	10.1±0.18	
$\chi_{2p,s}^{\text{O}(3)}$		22.9±0.3	20 ^a 21 ^b
$\chi_{2s,s}^{\text{O}(3)}$	0.557±0.007	1.113±0.013	
$\chi_{2p,s}^{\text{total}}$		27.5±0.3	25 ^a 25 ^b
$\chi_{2s,s}^{\text{total}}$		1.39±0.015	
Sr ₂ RuO ₄			
$\chi_{2p,a,b,s}^{\text{O}(1)}$	8.4±0.24	16.7±0.5	
$\chi_{2p,c,s}^{\text{O}(1)}$	6.8±0.23	13.6±0.5	
$\chi_{2p,s}^{\text{O}(1)}$		30.3±0.8	15 ^c 26 ^d 21 ^e
$\chi_{2s,s}^{\text{O}(1)}$	0.54±0.02	1.11±0.04	
$\chi_{2p,a,b,s}^{\text{O}(2)}$	1.2±0.24	5.0±0.9	3 ^c 4 ^d 4 ^e
$\chi_{2s,s}^{\text{O}(2)}$	0.16±0.024	0.33±0.05	
$\chi_{2p,s}^{\text{total}}$		35.3±1.2	18 ^c 29 ^d 25 ^e
$\chi_{2s,s}^{\text{total}}$		1.41±0.06	
Paramagnetic SrRuO ₃			
$\chi_{2p,s}^{\text{O}}$	3.6±0.5	22±3	21 ^f 30 ^g
$\chi_{2s,s}^{\text{O}}$	0.54±0.05	1.6±0.15	

^aReference 36.

^bTaken from figures in Ref. 31.

^cTaken from Fig. 3 in Ref. 14.

^dTaken from Fig. 2 in Ref. 37.

^eTaken from figures in Ref. 32.

^fRef. 38.

^gApproximate value in Ref. 39.

It is found that higher-dimensional members have a much smaller fraction of spin densities at the oxygen sites $\chi_{2p,s}^{\text{total}}/\chi_{\text{bulk},s}$, while the variation of the hole occupancies h_{2p}^{total} in Table II is small. Therefore, we can deduce that SrRuO_3 has a largely enhanced $D(E_F)$ especially at the ruthenium site because of the on-site Coulomb interactions at the ruthenium site. In a Stoner mechanism, the partially localized character of the $4d$ electrons and resulting narrow bands and high $D(E_F)$ are favorable for itinerant ferromagnetism and metamagnetism, as is systematically observed in $3d$ and $4d$ pure metals. The ferromagnetism of SrRuO_3 could be related to the smallness of the transferred spin density at the oxygen site.

In addition to the ferromagnetic fluctuations in $\text{Sr}_3\text{Ru}_2\text{O}_7$, incommensurate antiferromagnetic fluctuations were found,^{13,41} which are similar to those in Sr_2RuO_4 .⁴ These incommensurate antiferromagnetic fluctuations arise from the Fermi-surface nesting of one-dimensional Fermi-surface sheets, when the small spin density at the apical oxygen site weakens the transfer between RuO_2 layers, resulting in the low-dimensional character. We thus clarified the important roles of hole occupation and spin density in different oxygen orbitals and their relevance for the ferromagnetic and antiferromagnetic character of the ruthenates $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$.

IV. CONCLUSION

In conclusion, we have investigated microscopic hole occupancies and transferred spin densities at the oxygen sites by analyzing the ^{17}O NMR electric field gradients and anisotropic Knight shifts of $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ ($n=1, 2, \infty$). The hole occupancies at the oxygen sites are quite large, which is unexpected for a nondoped oxide. This gives evidence that the covalent character of the Ru-O bonding plays an important role in these compounds. The tilting (SrRuO_3) and the rotation ($\text{Sr}_3\text{Ru}_2\text{O}_7$) of the RuO_6 octahedra may account for

a weaker covalency, which originates from insufficient holes in the p_π antibonding orbitals which is not the case in the undistorted Sr_2RuO_4 .

The total spin densities at the oxygen sites derived from anisotropic ^{17}O Knight shifts are also high (20%–40% of the bulk spin susceptibility), which is, however, in good agreement with band-structure calculations and results obtained from polarized neutron experiments reported in the literature. Although the total oxygen hole occupancies per ruthenium atom do not significantly change among the series $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$, the spin densities at the oxygen sites decrease with increasing n . This suggests that higher-dimensional members of the series have narrower bands and, as a result, metamagnetism and itinerant ferromagnetism are induced in $\text{Sr}_3\text{Ru}_2\text{O}_7$ and SrRuO_3 , respectively. It is shown that the enhancement of the spin density at the oxygen site is comparable with that at the ruthenium site. The spin density at the apical oxygen site [O(2) in Sr_2RuO_4 , O(1) and O(2) in $\text{Sr}_3\text{Ru}_2\text{O}_7$] is much smaller than that at the in-plane oxygen site, which is responsible for the strong two-dimensional character in those compounds. The low dimensionality might lead to the occurrence of one-dimensional Fermi-surface nesting. This would explain the incommensurate antiferromagnetic fluctuations, which emerge in Sr_2RuO_4 and $\text{Sr}_3\text{Ru}_2\text{O}_7$. Structural distortions and magnetism in $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ are strongly related to the covalent character of the Ru $4d$ –O $2p$ molecular orbitals and the spin densities at the oxygen sites.

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