Planar CuO₂ hole density in high-*T_c* cuprates determined by NMR Knight shift: ⁶³Cu NMR on bilayered Ba₂CaCu₂O₄(F,O)₂ and three-layered Ba₂Ca₂Cu₃O₆(F,O)₂

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We report that planar CuO₂ hole densities in high- T_c cuprates are consistently determined by the Cu NMR Knight shift. In single- and bilayered cuprates, it is demonstrated that the spin part of the Knight shift $K_s(300 \text{ K})$ at room temperature monotonically increases with the hole density p from the underdoped to overdoped regions, suggesting that the relationship of $K_s(300 \text{ K})$ vs p is a reliable measure to determine p. The validity of this $K_s(300 \text{ K})$ -p relationship is confirmed by the investigation of the p dependencies of hyperfine magnetic fields and of spin susceptibility for single- and bilayered cuprates with tetragonal symmetry. Moreover, the analyses are compared with NMR data on three-layered Ba₂Ca₂Cu₃O₆(F,O)₂ and HgBa₂Ca₂Cu₃O_{8+ δ} and five-layered HgBa₂Ca₄Cu₅O_{12+ δ}, which suggests the general applicability of the $K_s(300 \text{ K})$ -p relationship to multilayered compounds with more than three CuO₂ planes. The measurement of $K_s(300 \text{ K})$ enables us to separately estimate p for each CuO₂ planes.

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I. INTRODUCTION

In hole-doped high- T_c cuprates, the hole density p in CuO₂ planes has been determined by various methods: indirect chemical methods like solid solutions,¹⁻⁴ bond valence sums determined from structural bond lengths,⁵⁻⁷ or the Fermi surface topology.⁸ Moreover, the thermoelectric power is a universal function of p,^{9,10} and the phase diagram for hole doped cuprates is well described by $T_c = T_{c,max}[1 - 82.6(p - p)]$ $(0.16)^2$,¹¹ which is applicable for the estimation of p when suitable structural data are not available. These methods are, however, inapplicable when we deal with multilayered compounds because they are composed of more than two inequivalent CuO₂ planes in a unit cell [see Fig. 3(a) as an example]. In multilayered cuprates, doped hole carriers are inequivalent between outer CuO₂ planes (OPs) and inner CuO₂ planes (IPs) due to the imbalance of the Madelung potential on each CuO₂ plane; the above-mentioned methods would not evaluate each hole density inherent to CuO₂ planes but a total hole density. Precise determination of hole density on respective CuO₂ planes is indispensable for gaining deep insight into the phenomena observed in multilayered cuprates.^{12–16}

It is known that the spin part of the Knight shift $K_s(300 \text{ K})$ at room temperature increases with p in hole-doped cuprates.^{13,17-22} The quantity $K_s(300 \text{ K})$ for OP and IP are separately determined by Cu NMR. Therefore, each value of p for OP and for IP can be estimated if the relationship between $K_s(300 \text{ K})$ and p is established. Meanwhile, a linear equation $p = 0.502K_s(300K) + 0.0462$ has been reported,^{13,23} where p was derived from the nuclear quadrupole resonance (NQR) frequencies of Cu and O in CuO₂ planes.²⁴ The values of p estimated by the linear equation, however, seem relatively large. For example, an optimal doping level has been evaluated to be $p \sim 0.22$ to 0.24 in five-layered Hg-based compounds,¹⁴ which is larger than a widely accepted optimal doping level in hole-doped cuprates of $p \sim 0.16$. This inconsistency is probably due, in part, to the calculation that connects NQR frequencies to p.²⁵ In addition to that, it is nontrivial whether the *p* dependence of $K_s(300 \text{ K})$ is described with a single equation which holds among different materials. K_s is proportional to spin susceptibility χ_s and hyperfine coupling constants A_{hf} as $K_s = A_{\text{hf}}\chi_s$, where the supertransferred magnetic field *B* in $A_{\text{hf}} = A + 4B$ depends on the materials.²⁶

In this paper, we report that the planar CuO₂ hole density *p* in high- T_c cuprates is consistently evaluated from the spin part of the ⁶³Cu Knight shift $K_s(300 \text{ K})$ at room temperature. We show the *p* dependencies of $K_s(300\text{ K})$ and of *B* in bilayered Ba₂CaCu₂O₄(F,O)₂ (0212F) together with those of other single- and bilayered materials with tetragonal symmetry. NMR data on three-layered Ba₂Ca₂Cu₃O₆(F,O)₂ (0223F) and HgBa₂Ca₂Cu₃O_{8+ $\delta}$} (Hg1223),²⁷ and five-layered HgBa₂Ca₄Cu₅O_{12+ δ} (Hg1245)²⁸ suggest that the *p* dependencies of $K_s(300 \text{ K})$ and of *B* hold in multilayered compounds as well. These results show that the present method, based on the Knight shift, enables us to separately estimate *p* for each CuO₂ plane in multilayered high- T_c cuprates.

II. EXPERIMENTAL DETAILS

Polycrystalline powder samples of Ba₂CaCu₂O₄(F,O)₂ (0212F) and Ba₂Ca₂Cu₃O₆(F,O)₂ (0223F), which are listed in Table I, were prepared by high-pressure synthesis, as described elsewhere.^{29–31} The crystal structures are shown in Figs. 1(a) and 3(a). Powder x-ray-diffraction analysis shows that these compounds comprise almost a single phase, and that the *a*-axis length continually decreases with an increase in the nominal fraction of $O^{2-.29} T_c$ was uniquely determined by the onset of superconducting (SC) diamagnetism using a dc superconducting quantum interference device (SQUID) magnetometer. Four 0212F samples exhibit a systematic change in T_c , as the nominal fraction of oxygen O^{2-} decreases at the apical fluorine F^{1-} sites (i.e., the hole-doping level

TABLE I. List of samples measured in this study, bilayered Ba₂CaCu₂O₄(F,O)₂ (0212F) and three-layered Ba₂Ca₂Cu₃O₆(F,O)₂ (0223F). T_c was determined by the onset of SC diamagnetism using a dc SQUID magnetometer. The values of *p* for 0212F are evaluated using $T_c = T_{c,max}[1 - 82.6(p - 0.16)^2]$.¹¹ For three-layered 0223F, the two values of $K_{s,ab}(300 \text{ K})$ and of *B* correspond to OP and IP, respectively.

Sample	$T_c(\mathbf{K})$	р	<i>K</i> _{<i>s</i>,<i>ab</i>} (300 K) (%)	B(kOe)
0212F(#1)	102	0.174	0.38	80
0212F(#2)	105	0.149	0.33	74
0212F(#3)	73	0.114	0.25	67
0212F(#4)	40	0.085	0.20	67
0223F	120		0.349, 0.275	72, 67

decreases). Note that the actual fraction of F^{1-} and O^{2-} is difficult to determine.^{29,32,33} In Table I, the hole density pis evaluated by using $T_c = T_{c,max}[1 - 82.6(p - 0.16)^2]$.¹¹ For NMR measurements, the powder samples were aligned along the *c* axis in an external field *H* of ~16 T and fixed by using stycast 1266 epoxy. The NMR experiments were performed by a conventional spin-echo method in the temperature (*T*) range of 4.2 to 300 K with *H* perpendicular or parallel to the *c* axis. The width of the first exciting $\pi/2$ pulse was 6 μ s. The external field *H* was calibrated by using the ²⁷Al free induction decay signal.

III. RESULTS

A. Bilayered Ba₂CaCu₂O₄(F,O)₂

1. ⁶³Cu NMR with $H \parallel ab$

Figure 1(b) shows a typical ⁶³Cu NMR spectrum of the central transition $(1/2 \Leftrightarrow -1/2)$ for 0212F(#1), which has the largest nominal O^{2-} composition among the bilayered samples used in this study. The field-swept NMR spectrum was measured at *H* perpendicular to the *c* axis ($H \parallel ab$). Here, the NMR frequency ω_0 was fixed at 174.2 MHz. According to second-order perturbation theory for the nuclear Hamiltonian,^{34,35} total NMR shifts consist of the Knight shift K_{ab} with $H \parallel ab$ and the second-order quadrupole shift:

$$\frac{\omega_0 - \gamma_N H_{\text{res}}}{\gamma_N H_{\text{res}}} = K_{ab} + \frac{3\nu_Q^2}{16(1 + K_{ab})} \frac{1}{(\gamma_N H_{\text{res}})^2}, \quad (1)$$

where γ_N is a nuclear gyromagnetic ratio, H_{res} is an NMR resonance field, and ν_Q is the nuclear quadrupole frequency. In order to subtract K_{ab} from the total NMR shift, we estimated ν_Q by NQR measurements at H = 0 T and T = 1.5 K. The NQR spectrum for 0212F(#1) is shown in Fig. 1(d), which has the ⁶³Cu and ⁶⁵Cu components. The quantity ⁶³ ν_Q of ⁶³Cu is estimated to be 16.5 MHz by the spectral fit shown in the figure. For other bilayered compounds, the values of ⁶³ ν_Q are 15.7, 13.7, and 12.5 MHz for 0212F(#2), (#3), and (#4), respectively.

Figure 2(a) shows the spin part of the Knight shift, $K_{s,ab}(T)$, as a function of temperature. The Knight shift K in high- T_c cuprates comprises a T-dependent spin part $K_s(T)$ and a T-independent orbital part K_{orb} as follows:



FIG. 1. (Color online) (a) Crystal structure of bilayered Ba₂CaCu₂O₄(F,O)₂ (0212F). The heterovalent substitution of O²⁻ for F¹⁻ increases the hole density. (b) ⁶³Cu NMR spectra for 0212F(#1) at T = 60 K with H perpendicular to the c axis ($H \parallel ab$). The dashed line points to K = 0. (c) ⁶³Cu NMR spectra for 0212F(#1) at T = 60 K with H parallel to the c axis ($H \parallel c$). The peak marked with an asterisk (*) is from unoriented grains with $\theta \sim 90^{\circ}$, where θ is the angle between H and the c axis. If θ in the unoriented grains were distributed completely randomly, the peak (*) could coincide with the spectral peak in (b). (d) Cu NQR spectrum at T = 1.5 K. The spectrum is composed of ⁶³Cu and ⁶⁵Cu.

where α is the direction of *H*. We estimate $K_{\text{orb},ab} \simeq 0.23\%$, assuming $K_{s,ab} \simeq 0$ at the T = 0 limit. The value of $K_{\text{orb},ab}$ is consistent with that in other hole-doped high- T_c cuprates.^{17,20,21,36} Upon cooling down to T_c , $K_{s,ab}(T)$ is roughly constant for 0212F(#1), while $K_{s,ab}(T)$ decreases for the other four samples in association with the opening of pseudogaps.^{37,38} It is well known that the pseudogaps in $K_{s,ab}(T)$ emerge in underdoped regions, not in overdoped regions.^{20,36} A steep decrease below T_c for all samples indicates the reduction in spin susceptibility $\chi_s(T)$ proportional to $K_{s,ab}(T)$ due to the formation of spin-singlet Cooper pairing. We note here that, in hole-doped cuprates, $K_{s,ab}(T)$ at room temperature, $K_{s,ab}(300$ K), increases with hole density p.^{13,17–22} The values of $K_{s,ab}(300$ K) in the 0212F samples are listed in Table. I. The relationship between p and $K_{s,ab}(300$ K) is discussed later.

2. ⁶³Cu NMR with $H \parallel c$

Figure 1(c) shows a typical Cu NMR spectrum of the central transition $(1/2 \Leftrightarrow -1/2)$ for 0212F(#1), where the field-swept NMR spectra were measured with *H* parallel to the *c* axis $(H \parallel c)$ and at $\omega_0 = 174.2$ MHz. The small peak denoted by



FIG. 2. (Color online) (a) Spin part of the ⁶³Cu Knight shift $K_{s,ab}(T)$ with $H \parallel ab$ as a function of temperature. The data are assigned as labeled in the figure. (b) Spin part of the ⁶³Cu Knight shift $K_{s,c}(T)$ with $H \parallel c$. $K_{s,c}(T)$ shows a T dependence similar to that of $K_{s,ab}(T)$.

the asterisk (*) in the higher-field region arises from unoriented grains with $\theta \sim 90^{\circ}$, where θ is the angle between H and the c axis.

Figure 2(b) shows the *T*-dependence of $K_{s,c}(T)$. We estimate $K_{\text{orb},c} \simeq 1.22\%$, assuming $K_{s,c} \simeq 0$ at the T = 0 limit. Note that when $H \parallel c$ axis, the second-order quadrupole shift, corresponding to the second term in Eq. (1), is zero.^{34,35} The quantity $K_{s,c}(T)$ in Fig. 2(b) shows a similar *T*-dependence with $K_{s,ab}(T)$ in Fig. 2(a), as reported for other compounds such as Tl-,^{21,39} Bi-,¹⁹ and Hg-based compounds.^{27,40} It is, however, different from L214,¹⁸ YBa₂Cu₃O_{6+x} (Y123),^{17,41,42} and YBa₂Cu₄O₈ (Y124)⁴³; $K_{s,c}(T)$ increases below T_c upon cooling. This inconsistency comes from the difference of hyperfine magnetic fields discussed below.

3. Hyperfine magnetic field in CuO₂ plane

According to the Mila-Rice Hamiltonian,²⁶ the spin Knight shift of Cu in the CuO₂ plane is expressed as

$$K_{s,\alpha}(T) = (A_{\alpha} + 4B)\chi_s(T) (\alpha = c, ab), \qquad (3)$$

where A_{α} and B are the onsite and the supertransferred hyperfine fields of Cu, respectively. Here, the A_{α} consists of the contributions induced by onsite Cu $3d_{x^2-y^2}$ spins—anisotropic dipole, spin-orbit, and isotropic core polarization; the value of B originates from the isotropic 4s spin polarization produced by neighboring four Cu spins through the Cu($3d_{x^2-y^2}$)-O($2p\sigma$)-Cu(4s) hybridization. Since the spin susceptibility $\chi_s(T)$ is assumed to be isotropic, the anisotropy Δ of $K_{s,\alpha}(T)$ is given by

$$\Delta \equiv \frac{K_{s,c}(T)}{K_{s,ab}(T)} = \frac{A_c + 4B}{A_{ab} + 4B}.$$
(4)

From Fig. 2, Δ is evaluated to be ~0.42, 0.38, 0.33, and 0.33 for 0212F(#1), 0212F(#2), 0212F(#3), and 0212F(#4), respectively. The onsite hyperfine fields, $A_{ab} \sim 37$ kOe/ μ_B and $A_c \sim -170$ kOe/ μ_B ,^{44–46} are assumed to be material-independent in hole-doped high- T_c cuprates, which allows us to estimate *B* for 0212F samples as listed in Table I. These *B* values are larger than $B \sim 40$ kOe/ μ_B , which is a typical value for L214,¹⁸ Y123,^{17,41,42} and Y124⁴³ compounds.

B. Three-layered Ba₂Ca₂Cu₃O₆(F,O)₂

Figures 3(b) and 3(c) show Cu NMR spectra of the central transition $(1/2 \Leftrightarrow -1/2)$ for three-layered Ba₂Ca₂Cu₃O₆(F,O)₂ (0223F) at T = 200 K. The field-swept NMR spectra in Figs. 3(a) and 3(b) were measured at $H \parallel ab$ and $H \parallel c$, respectively. Here, the NMR frequency ω_0 was fixed at 174.2 MHz. As shown in the crystal structure of 0223F in Fig. 3(a), multilayered compounds, which have more than three CuO₂ planes in a unit cell, are composed of two kinds of CuO₂ planes: outer CuO₂ plane (OP) and inner CuO₂ plane (IP). The NMR spectra in Figs. 3(b) and 3(c) were assigned to OP and IP as denoted in the figure according to the literature.⁴⁷ The NMR spectral width for OP is much broader than that for IP; OP is closer to the Ba-F layer [see Fig. 3(a)], which is the source of the disorder due to the atomic substitution at apical-F sites.

Figures 3(d) and 3(e) show the *T* dependencies of $K_{s,ab}(T)$ and $K_{s,c}(T)$ for 0223F, respectively. Above $T_c = 120$ K, both $K_{s,ab}$ and $K_{s,c}$ decrease upon cooling *T* due to the opening of pseudogaps, which suggests that both OP and IP are underdoped. As mentioned before in connection with Fig. 2(a), $K_{s,ab}(300 \text{ K})$ increases with *p*. Therefore, Fig. 3(d) suggests that *p*(OP) is larger than *p*(IP) in 0223F. The estimation of hole density in multilayered cuprates is discussed later. The anisotropy Δ is evaluated from $K_{s,ab}(T)$ and $K_{s,c}(T)$ [see Eq. (4)], as conducted in the bilayered 0212F samples. Δ (OP) and Δ (IP) are evaluated to be ~0.36 and ~0.32, which gives $B(OP) \sim 72 \text{ kOe}/\mu_B$ and $B(IP) \sim 67 \text{ kOe}/\mu_B$.

IV. DISCUSSIONS

A. *p* dependence of $K_{s,ab}$ (300 K), *B*, and χ_s (300 K) in plane Cu site

Figure 4(a) shows $K_{s,ab}(300 \text{ K})$ for 0212F, Bi₂Sr₂CaCu₂O₈ (Bi2212),³⁶ Tl₂Ba₂CuO_{6+ $\delta}} (Tl2201),⁴⁸ and TlSr₂CaCu₂O_{7-<math>\delta}$ (Tl1212)²¹ plotted against p, which is evaluated by using $T_c = T_{c,\max}[1 - 82.6(p - 0.16)^2]$.¹¹ We note that those compounds have one or two CuO₂ planes with tetragonal symmetry, which are the homologous series of the apical-F-, Tl-, and Hg-based multilayered compounds. As shown in Fig. 4(a), $K_{s,ab}(300 \text{ K})$ monotonically increases with p from the underdoped to overdoped regions. $K_{s,ab}(300 \text{ K})$ seems material-independent, suggesting that $K_s(300 \text{ K})$ is a good indication of p in hole-doped cuprates. If the validity of the $K_{s,ab}(300 \text{ K})$ -p}</sub>



FIG. 3. (Color online) (a) Crystal structure of three-layered Ba₂Ca₂Cu₃O₆(F,O)₂ (0223F). In a unit cell, there are two kinds of CuO₂ planes: outer CuO₂ plane (OP) and inner CuO₂ plane (IP). (b), (c) Cu NMR spectrum of 0223F at T = 200 K with $H \parallel ab$ and $H \parallel c$. The spectra have two components arising from OP and IP. (d) ,(e) *T* dependencies of $K_{s,ab}(T)$ and $K_{s,c}(T)$ for 0223F.

relationship is presented, we can apply it to the estimation of *p* in multilayered compounds.

According to Eq. (3), the p dependence of $K_{s,ab}(300 \text{ K})$ is derived from those of B and $\chi_s(300 \text{ K})$. Figure 4(b) shows the p dependence of B for the same materials shown in Fig. 4(a).^{21,36,48} As presented in Fig. 4(b), B increases with p, showing a steep increase at $p \sim 0.18$ to 0.20. It is remarkable that the B term exhibits weak p dependence in the underdoped region while it shows a steep increase with p > 0.16 in the overdoped region. The *B* term arises from the Cu($3d_{x^2-v^2}$)-O($2p\sigma$)-Cu(4s) covalent bonds with the four nearest neighbor Cu sites; therefore, it is expected that the hybridization between the Cu($3d_{x^2-v^2}$) and O($2p\sigma$) orbits becomes larger as p increases in an overdoped regime and that, as a result, T_c starts to decrease. In Fig. 4(b), the *p*-dependent *B* term seems material-independent; however, the B terms for L214, Y123, and Y124 (~40 kOe/ μ_B), are relatively small compared with the values shown in Fig. 4(b). This inconsistency is seen in the variation of ${}^{63}\nu_0$ in Fig. 5 as well. The quantity ${}^{63}\nu_Q$ increases with p for all materials while, for a given p, the absolute values for L214 and Y123 are about 2 to 3 times larger than those for others. The values of ${}^{63}\nu_0$ depend on the hole number n_d in the Cu($3d_{x^2-y^2}$) orbit and n_p in the O(2p σ) orbit. Therefore, it is expected that n_d and n_p in L214 and Y123 are distributed in a manner different from those in the cuprates presented here, even though $p (p = n_d + 2n_p - 1)$ is the same between the former and the latter. Actually, it has been reported that n_d is large in L214 and Y123, which is the reason for the large value of ν_Q .^{24,25} In this context, it is considered that the hybridization between the Cu($3d_{x^2-y^2}$) and O($2p\sigma$) orbits in L214, Y123, and Y124 is smaller than those in the cuprates presented here, resulting in *B* for the former being remarkably smaller than for the latter. This is probably related to the crystal structures; L214, Y123, and Y124 have orthorhombic crystal structures in the SC region while 0212F, Bi2212, TI2201, and TI1212 have tetragonal structures. We conclude that the *p* dependence of *B* in Fig. 4(b) holds in CuO₂ planes with tetragonal symmetry.

Figure 4(c) shows the *p* dependence of $\chi_s(300 \text{ K})$, evaluated using $K_{s,ab}(300K) = |A_{ab} + 4B|\chi_s(300 \text{ K})$ [see Eq. (3)]. The quantity $\chi_s(300 \text{ K})$ increases with *p* and is nearly constant above $p \sim 0.20$ to 0.25, which is consistent with previous reports.⁵² In general, the spin susceptibility χ_s is related to the density of states at the Fermi level. Therefore, the reduction of $\chi_s(300 \text{ K})$ in an underdoped regime would be attributed to the emergence of pseudogaps as discussed in previous reports.⁵²

When we take into account the *p* dependencies of *B* and $\chi_s(300 \text{ K})$, the *p* dependence of $K_{s,ab}(300 \text{ K})$ —a monotonically increasing function—is explained. In overdoped regimes, a strong hybridization between the Cu $(3d_{x^2-y^2})$ and O $(2p\sigma)$ orbits increases the value of *B*, making $K_{s,ab}(300 \text{ K})$ larger as *p* increases. In underdoped regimes, the opening



FIG. 4. (Color online) (a) $K_{s,ab}(300 \text{ K})$ and (b) *B* plotted as a function of *p* for 0212F (\Box), Bi2212 (+), Tl2201 (\triangle), and Tl1212 (\bigcirc). The values of *p* are estimated from $T_c = T_{c,\max}[1 - 82.6(p - 0.16)^2]$.¹¹ The plots denoted by crosses (×) in (b) are for multi-layered compounds, which are listed in Table II. (c) *p* dependence of $\chi_s(300 \text{ K})$ evaluated from $K_{s,ab} = (A_{ab} + 4B)\chi_s$ [Eq. (3)]. The solid lines in the figures are to guide the eye.

TABLE II. List of $K_{s,ab}(300 \text{ K})$, p', and B for multilayered compounds: three-layered 0223F and Hg1223²⁷ and five-layered Hg1245.²⁸ Here, p' is the hole density that is tentatively evaluated by using experimental values of $K_{s,ab}(300 \text{ K})$ and the solid line in Fig. 4(a).

Sample, T_c	layer	$K_{s,ab}(300 \text{ K}) (\%)$	p'	$B(\mathrm{kOe}/\mu_B)$
0223F, 120 K	OP	0.35	0.156	72
	IP	0.28	0.115	67
Hg1223, 133 K	OP	0.41	0.185	90
	IP	0.32	0.139	80
Hg1245, 108 K	OP	0.34	0.151	74
	IP	0.21	0.075	61

of the pseudogap decreases $\chi_s(300 \text{ K})$, making $K_{s,ab}(300 \text{ K})$ smaller as *p* decreases. As a result, we conclude that the *p* dependence of $K_{s,ab}(300 \text{ K})$ holds in CuO₂ planes with tetragonal symmetry. This relationship between $K_{s,ab}(300 \text{ K})$ and *p* gives us an opportunity to determine *p* separately for OP and IP in multilayered cuprates, if it is confirmed that the relationship holds in multilayered cuprates.

B. Hole density estimation in multilayered compounds

In multilayered cuprates, doped hole carriers reside on OP and IP with different doping levels, and the CuO₂ layers show different physical properties due to the charge distribution, even in the same sample. Therefore, it is required to separately estimate *p* for OP and IP in order to study the electronic states of multilayered cuprates. It is invalid to apply the estimation methods used in single- and bilayered compounds; for example, the relationship $T_c = T_{c,max}[1 - 82.6(p - 0.16)^2]$,¹¹ the thermoelectric power,^{9,10} and the bond valence sums.^{5–7} Those methods are applicable to evaluate total hole density, but not to evaluate the hole density at each CuO₂ plane. On the other hand, Cu NMR measures the respective values of $K_{s,ab}(300 \text{ K})$ for OP and IP. If the $K_{s,ab}(300 \text{ K})$ -*p* relationship in Fig. 4(a) holds even in multilayered cuprates, it allows us to



FIG. 5. (Color online) ⁶³Cu NQR frequency ⁶³ ν_Q for holedoped cuprates, 0212F, Bi2212,³⁶ Tl2201,⁴⁹ Tl1212,²¹ L214,¹⁸ and Y123.^{50,51} Here, *p* is evaluated from the Sr-content *x* for L214 and from $T_{c,\max}$ ¹¹ for Y123. The solid lines in the figure are to guide the eye.

separately estimate p for OP and IP from experimental values of $K_{s,ab}(300 \text{ K})$.

Table II lists $K_{s,ab}(300 \text{ K})$, p', and B for multilayered cuprates: three-layered 0223F and HgBa₂Ca₂Cu₃O_{8+δ} $(Hg1223)^{27}$ and five-layered HgBa₂Ca₂Cu₃O_{12+ δ} (Hg1245).² Here, p' is the hole density tentatively estimated by using the $K_{s,ab}(300 \text{ K})$ -p relationship in Fig. 4(a). We plot B for those compounds as crosses (\times) in Fig. 4(b). The data plots fit into the other data, suggesting that the $K_{s,ab}(300 \text{ K})$ -p relationship is also valid in multilayered cuprates. We may consider the case that the $K_{s,ab}(300 \text{ K})$ -p relationship is modified in multilayered cuprates. According to Eq. (3), the possible source of the modification is the p dependence of B or of χ_s or both. Experimental B values in multilayered compounds, however, fall on the same universal curve as shown in Fig. 4(b); some unexpected modifications on the side of χ_s can indeed be considered as unlikely. Therefore, we conclude that the $K_{s,ab}(300 \text{ K})$ -p relationship in Fig. 4(a) is valid for CuO₂ planes in multilayered compounds, regardless of OP and IP.

Moreover, when we apply the $K_{s,ab}(300 \text{ K})$ -p relationship to five-layered compounds, the fact that the maximum T_c takes place at $p \sim 0.16^{14}$ supports the validity of the application to multilayered compounds. Several attempts have been used to determine p for hole-doped cuprates so far—the relationship between p and $K_{s,ab}(300 \text{ K})$ in this work is a promising approach to estimate p, which is applicable to multilayered compounds. Thus, this method allows the separate determination of p for OP and IP in multilayered compounds with a reliable accuracy.

V. CONCLUSION

We have shown that the planar CuO₂ hole densities p in high- T_c cuprates are consistently determined with the Cu NMR Knight shift. It has been demonstrated that the spin part of the Knight shift $K_{s,ab}(300 \text{ K})$ at room temperature is material-independent in CuO₂ planes with tetragonal symmetry and that $K_{s,ab}(300 \text{ K})$ monotonically increases with p from underdoped to overdoped regions. These observations suggests that $K_{s,ab}(300 \text{ K})$ is a reliable method for determining planar CuO₂ hole densities. The experimental values of $K_{s,ab}(300 \text{ K})$ and of hyperfine magnetic fields for three-layered Ba₂Ca₂Cu₃O₆(F,O)₂ and other multilayered compounds support the application of the p- $K_s(300 \text{ K})$ relationship to multilayered compounds. Thus, this relationship allows the separate determination of p for OP and IP in multilayered compounds with a reliable accuracy.

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