Knight shift vs hole concentration in Hg1201 and Hg1212

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We studied the hole concentration dependences of ^{63}Cu Knight shifts in single-CuO$_2$-layer high-T_c cuprate superconductors HgBa$_2$CuO$_{4+\delta}$ and double-layer HgBa$_2$CaCu$_2$O$_{6+\delta}$. We found that the spin Knight shift at room temperature as a function of the hole concentration in the single-layer superconductor is different from that in the double-layer superconductor. Two type relations between the spin Knight shift and the hole doping level serve to estimate the individual hole concentrations of the non-equivalent CuO$_2$ planes in a unit cell.

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I. INTRODUCTION

The doped hole carriers have been believed to distribute nonuniformly in the multi-layer cuprate superconductors. How to estimate the individual carrier doping levels of the non-equivalent CuO$_2$ planes in the multi-layer superconductors has been an issue. The bond valence sum associated with a local ionic valence has served to estimate the hole concentration [1–3]. The bond valence sum is a microscopic characterization based on the nanometer-scale structural analysis of the ionic bonds. Although a bulk observable such as thermoelectric power (Seebeck coefficient) at room temperature has been proposed to estimate the hole concentration [4], no macroscopic observables enable us to estimate the layer-selective hole concentration in the multi-layer systems. Then, microscopic observables have been desired.

The ab-plane spin component of the plane-site ^{63}Cu Knight shift $^{63}K_s^{ab}$ at room temperature was used to estimate the individual hole concentrations of the non-equivalent CuO$_2$ planes in the multi-layer superconductors [5, 6]. The hole concentration p is defined by the fraction of holes per Cu^{2+p} ion in the CuO$_2$ plane. A one-to-one correspondence between $^{63}K_s^{ab}$ and the hole concentration p has been proposed except for La$_{2-x}$Sr$_x$CuO$_4$ (LSCO), YBa$_2$Cu$_3$O$_{7-\delta}$ (Y1237) and YBa$_2$Cu$_4$O$_8$ (Y1248) [5, 6]. The single universal relation between $^{63}K_s^{ab}$ and p has bee adopted for the multi-layer superconductors. However, the uniform spin susceptibilities per Cu spin in single-layer systems are known to be larger than those in double-layer systems [7, 8]. It should be noted that the difference in $^{63}K_s^{ab}$ of single-CuO$_2$-layer superconductor HgBa$_2$CuO$_{4+\delta}$ (Hg1201) and double-layer HgBa$_2$CaCu$_2$O$_{6+\delta}$ (Hg1212) in [9–11] has been overlooked. Thus, an issue how relevant the application of the single universal relation between $^{63}K_s^{ab}$ and p is for the multi-layer systems should be addressed.

The optimal T_c's of Hg1201 and Hg1212 are the highest among the single-layer and the double-layer systems. The structural flatness of the CuO$_2$ plane characterizes Hg1201 and Hg1212. Figure 1 shows the schematic crys-
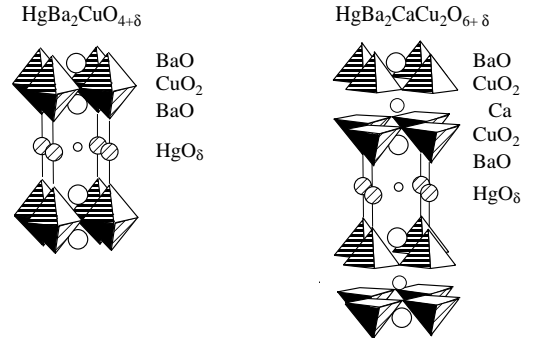

FIG. 1: Schematic crystal structures of Hg1201 (left) and Hg1212 (right).

tal structures of Hg1201 and Hg1212. The oxygen concentration in the HgO layer controls the hole doping level in the CuO$_2$ plane. The crystal symmetry is tetragonal. We believe that Hg1201 and Hg1212 are the canonical high-T_c cuprate superconductors.

In this paper, we studied the hole concentration dependences of the spin Knight shifts at room temperature in the single-layer superconductors Hg1201 and the double-layer Hg1212 in [9–11]. The present analysis is based on the NMR results reported in [9–11]. The preparation methods of the samples for the NMR measurements are described in [9, 10, 12]. We emphasize that the spin Knight shift as a function of the hole concentration in the single-layer superconductors is different from that in the double-layer superconductors

II. EXPERIMENTAL KNIGHT SHIFTS OF HG1201 AND HG1212

Figure 2 shows the ^{63}Cu Knight shifts $^{63}K^{ab}$'s of Hg1201 (open symbols) and Hg1212 (closed symbols) in an external magnetic field along the ab planes, which are reproduced from [9–11]. The doping levels are catego-
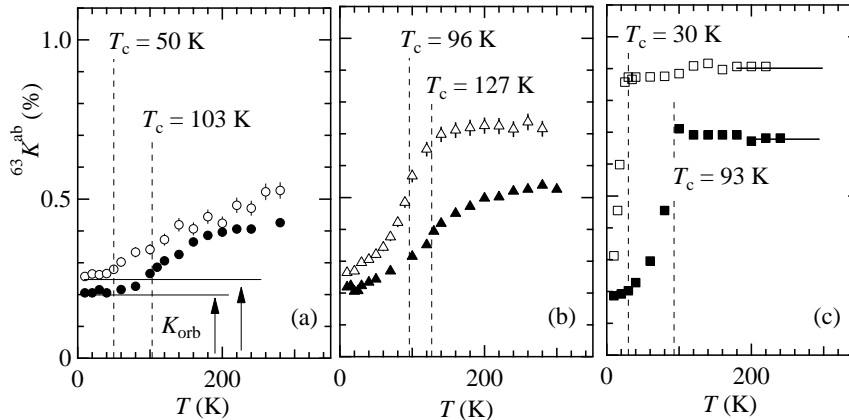
FIG. 2: ^{63}Cu Knight shifts $^{63}K^{ab}$ for Hg1201 (open symbols) and Hg1212 (closed symbols) in the underdoped (a), the optimally doped (b), and the overdoped regimes (c), which are reproduced from [9–11]. The dashed lines indicate the individual T_c 's. The sold lines in (c) are visual guides.

rized into underdoping (a), optimally doping (b), and overdoped doping (c).

The ^{63}Cu Knight shift $^{63}K^{ab}$ is given by $^{63}K^{ab} = {}^{63}K_s^{ab}(T) + {}^{63}K_{orb}^{ab}$, where $^{63}K_s^{ab}$ is the spin Knight shift and $^{63}K_{orb}^{ab}$ is the orbital shift. $^{63}K_s^{ab}$ is proportional to the uniform spin susceptibility multiplied by the hyperfine coupling constant. $^{63}K_{orb}^{ab}$ is proportional to the Van Vleck orbital susceptibility. The temperature dependence of $^{63}K^{ab}$ in the cuprate superconductors comes from that of the spin shift $^{63}K_s^{ab}$. We have estimated $^{63}K_{orb}^{ab} \sim 0.25$ % for Hg1201 and ~ 0.20 % for Hg1212 [9–11]. As seen in Fig. 2, $^{63}K_s^{ab}$ of Hg1201 is larger than that of Hg1212 at each doping regime.

Figure 3 shows the hole concentration p_h in [12] against $^{63}K_s^{ab}$ (%) at room temperature of Hg1201 and Hg1212 in [9–11]. From the least squares fits, we obtained two relations of S1: $p_h = 0.63\,{}^{63}K_s^{ab}(\mathrm{RT}) - 0.13$ (Hg1201) and D1, $p_h = 0.74\,{}^{63}K_s^{ab}(\mathrm{RT}) - 0.04$ (Hg1212). The solid lines in Fig. 3 indicate the fit functions of S1 and D1. The extrapolations of S1 and D1 to $p_h = 0$ lead to $^{63}K_s^{ab} = 0.21$ % (Hg1201) and $^{63}K_s^{ab} = 0.05$ % (Hg1212) at the phase boundary. The empirical functions of S1 and D1 are different from the previous fit functions F1 and F2 ($^{63}K_s^{ab} < 0.5$ %) adopted for the multi-layer systems in [5].

III. DISCUSSIONS

We discuss the hole concentration dependence upon the spin Knight shift for the other cuprate superconductors and the alternative estimation of the hole concentration.

Figure 4(a) shows p_h against $^{63}K_s^{ab}$ (%) of Hg1201, LSCO [13]; Hg1212, Y1237 [14, 15] and Y1248 [16–18]. We estimated $^{63}K_s^{ab}$ at room temperature for LSCO by
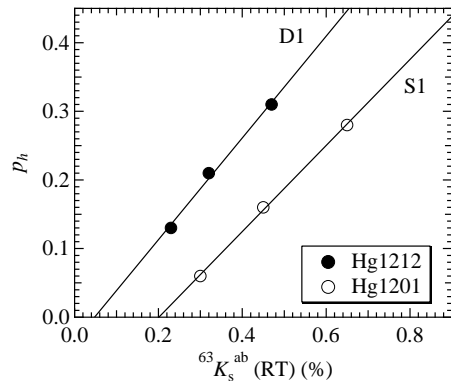

FIG. 3: Hole concentration p_h against spin Knight shift $^{63}K_s^{ab}$ at room temperature (RT) in Hg1201 and Hg1212. The solid lines are the fit functions of S1: $p_h = 0.63\,{}^{63}K_s^{ab}(\mathrm{RT}) - 0.13$ (Hg1201) and D1, $p_h = 0.74\,{}^{63}K_s^{ab}(\mathrm{RT}) - 0.04$ (Hg1212).

linear extrapolation from the existing data in [13]. The single-layer system LSCO is located close to S1. The double-layer systems of Y1237 and Y1248 are located close to the line D1.

In Fig. 4(b), we estimated the hole concentrations p 's by the parabolic curve of $T_c/T_{c,\max} = 1 - 82.6(p - 0.16)^2$ in [19] after [5]. Figure 4(b) shows p against $^{63}K_s^{ab}$ (%) of Hg1201, LSCO [13], $Tl_2Ba_2CuO_{6+\delta}$ (Tl2201) [20]; Hg1212, and $Ba_2CaCu_2O_4(F,O)_2$ (0212F) [6]. In spite of the alternative estimation of the hole concentration, the p vs $^{63}K_s^{ab}$ dependence of Hg1201 is different from that of Hg1212. The reason why $^{63}K_s^{ab}$'s of Hg1212 are smaller than those of Hg1201 at the respective doping levels in Figs. 2 and 3 may be due to the effect of the magnetic bi-
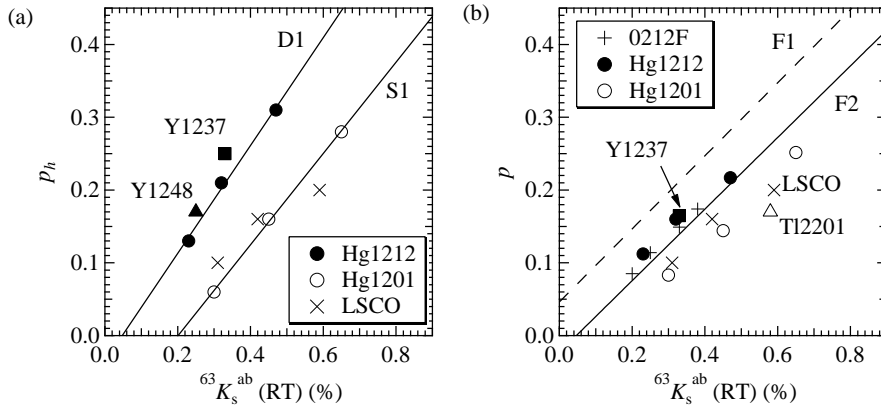
FIG. 4: (a) Hole concentration p_h against spin Knight shift $^{63}K_s^{ab}$ of Hg1201, LSCO [13]; Hg1212, Y1237 [14, 15] and Y1248 [16–18]. (b) Hole concentration p against spin Knight shift $^{63}K_s^{ab}$ of Hg1201, LSCO [13], Tl2201 [20]; Hg1212, 0212F [6]. One should note p_h (a) and p (b) estimated from the different ways. In (b), F1 (dashed line) and F2 (sold line) are the previous functions for $^{63}K_s^{ab} < 0.5$ % in [5].

layer coupling. The effect of the bilayer coupling has also been studied for the triple-layer superconductors. Thus, one should take into consideration which type relation is relevant S1 or D1 to estimate the individual hole concentrations of the non-equivalent CuO$_2$ planes in the multi-layer superconductors.

IV. CONCLUSION

We found that the spin Knight shift $^{63}K_s^{ab}$ as a function of the hole concentration p_h in the single-layer super-

conductors Hg1201 is different from that in the double-layer superconductors Hg1212. Since we believe that Hg1201 and Hg1212 are the canonical systems, the p_h dependences upon $^{63}K_s^{ab}$ at room temperature in Hg1201 and Hg1212 should be standard to estimate the individual hole concentrations of the non-equivalent CuO$_2$ planes in a unit cell.

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