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## Knight shift vs hole concentration in Hg1201 and Hg1212

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*Department of Physics, Graduate School of Science, Kyoto Sangyo University, Kamigamo-Motoyama, Kita-ku, Kyoto 603-8555, Japan***Abstract**

We studied the hole concentration dependences of  $^{63}\text{Cu}$  Knight shifts in single- $\text{CuO}_2$ -layer high- $T_c$  cuprate superconductors  $\text{HgBa}_2\text{CuO}_{4+\delta}$  and double-layer  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$ . 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  $\text{CuO}_2$  planes in a unit cell.

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**Keywords:** NMR; Knight shift; Hg-based superconductor; hole concentration

**1. 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  $\text{CuO}_2$  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  $^{63}\text{Cu}$  Knight shift  $^{63}K_s^{ab}$  at room temperature was used to estimate the individual hole concentrations of the non-equivalent  $\text{CuO}_2$  planes in the multi-layer superconductors [5, 6]. The hole concentration  $p$  is defined by the fraction of holes per  $\text{Cu}^{2+p}$  ion in the  $\text{CuO}_2$  plane. A one-to-one correspondence between  $^{63}K_s^{ab}$  and the hole concentration  $p$  has been proposed except for  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  (LSCO),  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (Y1237) and  $\text{YBa}_2\text{Cu}_4\text{O}_8$  (Y1248) [5, 6]. The single universal relation between  $^{63}K_s^{ab}$  and  $p$  has been 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- $\text{CuO}_2$ -layer superconductor  $\text{HgBa}_2\text{CuO}_{4+\delta}$  (Hg1201) and double-layer  $\text{HgBa}_2\text{CaCu}_2\text{O}_{6+\delta}$  (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.

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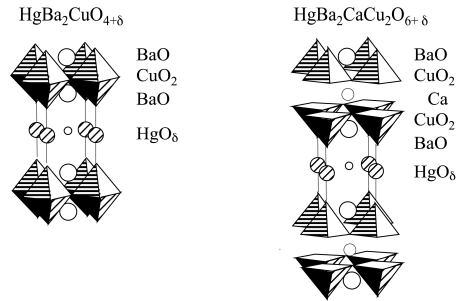


Fig. 1. Schematic crystal structures of Hg1201 (left) and Hg1212 (right).

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  $\text{CuO}_2$  plane characterizes Hg1201 and Hg1212. Figure 1 shows the schematic crystal structures of Hg1201 and Hg1212. The oxygen concentration in the HgO layer controls the hole doping level in the  $\text{CuO}_2$  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 experiments 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.

## 2. Experimental Knight shifts of Hg1201 and Hg1212

Figure 2 shows the  $^{63}\text{Cu}$  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 categorized into underdoping (a), optimally doping (b), and overdoped doping (c).

The  $^{63}\text{Cu}$  Knight shift  $^{63}K^{ab}$  is given by  $^{63}K^{ab} = ^{63}K_s^{ab}(T) + ^{63}K_{\text{orb}}^{ab}$ , where  $^{63}K_s^{ab}$  is the spin Knight shift and  $^{63}K_{\text{orb}}^{ab}$  is the orbital shift.  $^{63}K_s^{ab}$  is proportional to the uniform spin susceptibility multiplied by the hyperfine coupling constant.  $^{63}K_{\text{orb}}^{ab}$  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  $^{63}K_{\text{orb}}^{ab} \sim 0.25\%$  for Hg1201 and  $\sim 0.20\%$  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.

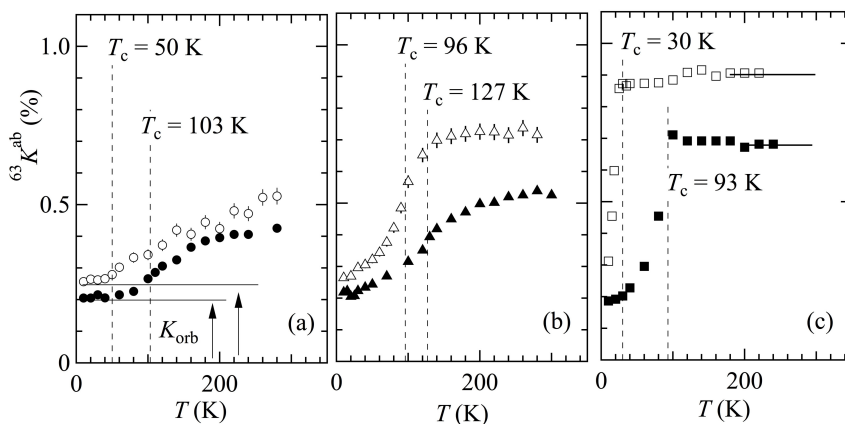


Fig. 2.  $^{63}\text{Cu}$  Knight shifts  $^{63}K^{ab}$  for Hg1201 (open symbols) and Hg1212 (closed symbols) in the underdoped (a), the optimally doped (b), and the overdoped regimes (c), which are reproduced from [9-11]. The dashed lines indicate the individual  $T_c$ 's. The solid lines in (c) are visual guides.

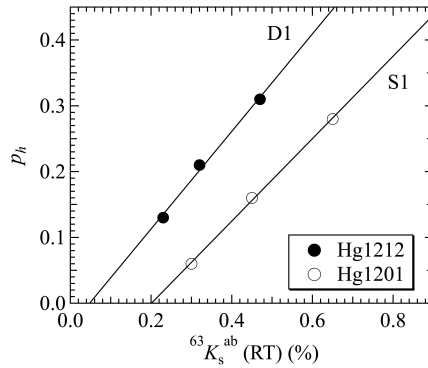


Fig. 3. Hole concentration  $p_h$  against spin Knight shift  ${}^{63}K_s^{ab}$  at room temperature (RT) in Hg1201 and Hg1212. The solid lines are the fit functions of S1:  $p_h = 0.63{}^{63}K_s^{ab}(\text{RT}) - 0.13$  (Hg1201) and D1:  $p_h = 0.74{}^{63}K_s^{ab}(\text{RT}) - 0.04$  (Hg1212).

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:  $p_h = 0.63{}^{63}K_s^{ab}(\text{RT}) - 0.13$  (Hg1201) and D1:  $p_h = 0.74{}^{63}K_s^{ab}(\text{RT}) - 0.04$  (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].

### 3. 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 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  $T_c/T_{c,\text{max}} = 1 - 82.6(p - 0.16)^2$  in [19] after [5]. Figure 4(b) shows  $p$  against  ${}^{63}K_s^{ab}$  (%) of Hg1201, LSCO [13],  $\text{Ti}_2\text{Ba}_2\text{CuO}_{6+\delta}$  (Ti2201) [20]; Hg1212, and  $\text{Ba}_2\text{CaCu}_2\text{O}_4(\text{F},\text{O})_2$  (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 bilayer 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  $\text{CuO}_2$  planes in the multi-layer superconductors.

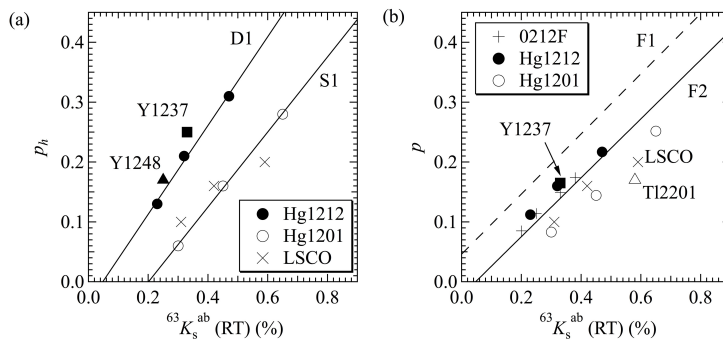


Fig. 4. (a) Hole concentration  $p_h$  against spin Knight shift  ${}^{63}K_s^{ab}$  of Hg1201, LSCO [13]; Hg1212, Y1237 [14, 15] and Y1248 [16-18]. (b) Hole concentration  $p$  against spin Knight shift  ${}^{63}K_s^{ab}$  of Hg1201, LSCO [13], Ti2201 [20]; Hg1212, 0212F [6]. One should note  $p_h$  (a) and  $p$  (b) estimated from the different ways. In (b), F1 (dashed line) and F2 (solid line) are the previous functions for  ${}^{63}K_s^{ab} < 0.5$  % in [5].

#### 4. Conclusions

We found that the spin Knight shift  $^{63}K_s^{ab}$  as a function of the hole concentration  $p_h$  in the single-layer superconductors 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  $\text{CuO}_2$  planes in a unit cell.

#### References

- [1] R. J. Cava, A. W. Hewat, E. A. Hewat, B. Batlogg, M. Marezio, K. M. Rabe, J. J. Krajewski, W. F. Peck Jr., L. W. Rupp Jr., *Physica C* 165 (1990) 419-433.
- [2] I. D. Brown, *J. Solid State Chem.* 90 (1991) 155-167.
- [3] Y. Tokura, J. B. Torrance, T. C. Huang, A. I. Nazzari, *Phys. Rev. B* 38 (1988) 7156-7159.
- [4] J. L. Tallon, C. Bernhard, H. Shaked, R. L. Hitterman, J. D. Jorgensen, *Phys. Rev. B* 51 (1995) 12911-12914.
- [5] H. Mukuda, S. Shimizu, A. Iyo, Y. Kitaoka, *J. Phys. Soc. Jpn.* 81 (2012) 011008.
- [6] S. Shimizu, S. Iwai, S. Tabata, H. Mukuda, Y. Kitaoka, P. M. Shirage, H. Kito, A. Iyo, *Phys. Rev. B* 83 (2011) 144523.
- [7] A. J. Millis, L. B. Ioffe, H. Monien, *J. Phys. Chem. Solids*, 56 (1995) 1641-1643.
- [8] A. J. Millis, H. Monien, *Phys. Rev. Lett.* 70 (1993) 2810-2813.
- [9] Y. Itoh, T. Machi, S. Adachi, A. Fukuoka, K. Tanabe, H. Yasuoka, *J. Phys. Soc. Jpn.* 67 (1998) 312-317.
- [10] Y. Itoh, A. Tokiwa-Yamamoto, T. Machi, K. Tanabe, *J. Phys. Soc. Jpn.* 67 (1998) 2212-2214.
- [11] Y. Itoh, T. Machi, in "Superconducting Cuprates: Properties, Preparation and Applications," ed. Koenraad N. Courtlandt (Nova Science Publisher, NY, 2009) p.p. 235 - 268.
- [12] A. Fukuoka, A. Tokiwa-Yamamoto, M. Itoh, R. Usami, S. Adachi, K. Tanabe, *Phys. Rev. B* 55 (1997) 6612-6620.
- [13] S. Ohsugi, Y. Kitaoka, K. Ishida, G.-q. Zheng, K. Asayama, *J. Phys. Soc. Jpn.* 63 (1994) 700-715.
- [14] M. Takigawa, P. C. Hammel, R. H. Heffner, Z. Fisk, J. L. Smith, R. B. Schwarz, *Phys. Rev. B* 39 (1989) 300-303.
- [15] T. Shimizu, H. Aoki, H. Yasuoka, T. Tsuda, Y. Ueda, K. Yoshimura, K. Kosuge, *J. Phys. Soc. Jpn.* 62 (1993) 3710-3720.
- [16] T. Machi, I. Tomeno, T. Miyatake, N. Koshizuka, S. Tanaka, T. Imai, H. Yasuoka, *Physica C* 173 (1991) 32-36.
- [17] H. Zimmermann, M. Mali, I. Mangelschots, J. Roos, L. Psuli, D. Brinkmann, J. Karpinski, S. Rusiecki, E. Kaldis, *J. Less-Common Metals*, 164&165 (1990) 138-145.
- [18] H. Zimmermann, M. Mali, M. Bankay, D. Brinkmann, *Physica C* 185-189 (1991) 1145-1146.
- [19] M. R. Presland, J. L. Tallon, R. G. Buckley, R. S. Liu, N. E. Flower, *Physica C* 176 (1991) 95-105.
- [20] S. Kambe, H. Yasuoka, A. Hayashi, Y. Ueda, *Phys. Rev. B* 47 (1993) 2825-2834.