PHYSICAL REVIEW B, VOLUME 65, 184504

Superconducting and magnetic characteristics in the multilayered high-T_c cuprates $TlBa_2Ca_2Cu_3O_{10-y}$ with $T_c > 130$ K probed by Cu and Tl NMR: High value for T_c

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(Received 7 November 2001; published 15 April 2002)

We report ^{63}Cu and ^{205}Tl nuclear magnetic resonance (NMR) measurements on trilayered high-T_c compounds $TlBa_2Ca_2Cu_3O_{10-y}$ (Tl-1223) that were synthesized at a high pressure and exhibits a high value of superconducting (SC) transition temperature $T_c > 130$ K. In the SC state, the nuclear spin-lattice relaxation rate $1/T_1$ reveals a T^3 behavior below T_c, followed by a $T_1T = \text{const}$ behavior at very low temperatures. The results are accounted for by the *d*-wave pairing model where the presence of the residual density of the states $N_{res}(E_F)$ is incorporated at the Fermi level to be consistent with the experiments. The important finding is that the size [in $N_{res}(E_F)$] is much smaller for the present compounds of Tl-1223 with $T_c > 130$ K than for the previous Tl-2223. Correspondingly, it is shown that an NMR intensity at a satellite peak in the Tl-NMR spectrum, which originates from a possible substitution of Tl for Ca, is much smaller for the former than for the latter. The synthesis technique at a high pressure is found to be a good way to remove such a crystal imperfection due to Tl/Ca intersubstitution. We have demonstrated from a microscopic point of view that as a result of decreasing the degree of disorder effect, the T_c in Tl-1223 has revealed a value higher than 130 K.

DOI: 10.1103/PhysRevB.65.184504 PACS number(s): 74.72.−h

I. INTRODUCTION

Since the discovery of high-T_c cuprates, extensive effort to raise a superconducting (SC) transition temperature T_c is being currently made, and the highest value of T_c to date reaches $T_c = 133$ K in $HgBa_2Ca_2Cu_3O_{8+y}$ (Hg-1223).[1] This record of T_c has, however, not yet been overcome out for a while in spite of extensive effort. On the other hand, a maximum T_c of $TlBa_2Ca_2Cu_3O_{10-y}$ (Tl-1223) system has been established to be about 125 K. However, recently Iyo *et al.* succeeded in synthesizing Tl-1223 and Tl-1234 that reveal $T_c = 133.5$ K and 127 K, respectively, using a high-pressure-synthesis (HPS) technique.[2,3] These values of T_c are comparable to the value for Hg-1223. Apparently, the HPS technique seems to be very efficient in raising a maximum value of T_c for Tl-1223 by about 10 K. It is, therefore, an important issue to be clarified why the HPS technique is so remarkable to raise the T_c and whether or not it leads to a promising route in order to obtain a further high T_c even for other materials.

These Hg- and Tl-1223 compounds have three sheets of CuO_2 planes in a unit cell, consisting of an inner square (IP) one and two outer pyramidal (OP) ones. Here the Cu site at the IP (OP) is surrounded by square (pyramidal) coordinated oxygen. It was reported that the respective local-hole doping levels N_h(IP) and N_h(OP) are different at the IP and OP, causing contrasting magnetic and SC behaviors.[4–6] From the previous nuclear-magnetic-resonance (NMR) studies of various multilayered compounds,[6] the N_h(IP) and N_h(OP) in Hg-1223 are nearly the same, both exhibiting almost optimal hole contents. This is a microscopic origin for the highest T_c in Hg-1223 to date. As the number of CuO_2 layers (n) increases from $n=3$ to either $n=4$ or 5, T_c is decreased. This was concluded because N_h(IP) remains either in an optimum-doping level or an underdoping level, but N_h(OP) is predominantly in an overdoped regime even though the total hole content is increased. In this context, it was suggested that the $T_c = 133$ K in Hg-1223 approaches a possible upper limit in high-T_c cuprates.[6]

It is important to investigate why the HPS technique makes the T_c in the Tl-1223's higher by more than 10 K and how different their magnetic and SC properties are from those in Hg-1223 with the highest value of T_c being 133 K to date. In this paper, we report ^{63}Cu- and ^{205}Tl-NMR measurements in Tl-1223 synthesized by the HPS technique (hereafter denoted as Tl-1223HPS). The NMR results reveal that the N_h(IP) and N_h(OP) in Tl-1223HPS are almost the same as in Hg-1223, and the magnetic characteristics in the IP and OP resemble those in Hg-1223, exhibiting a common feature associated with the development of an antiferromagnetic (AFM) spin fluctuations upon cooling. The nuclear spin-lattice relaxation rate $1/T_1$ being far below T_c reveals a $T_1T = \text{const}$ behavior due to the presence of the residual density of states $N_{res}(E_F)$ at the Fermi level. From a comparison with the available results for Hg-1223 (Ref. 7) and Tl-2223 (Refs. 8 and 9) that were synthesized by the standard technique, it is indicated that an extent of the crystal imperfection in Tl-1223HPS is similar to that in Hg-1223, but it is much smaller than that in Tl-2223 with the lower T_c. Although the charge reservoir layer of Tl-2223 is different from that of Tl-1223, they have a common feature that the starting composition is made nonstoichiometric as to obtain a high value of T_c. It is demonstrated from a microscopic point of view that the degree of disorder associated with some crystal inhomogeneity in Tl-1223HPS is much less than that in Tl-2223. We conclude that the HPS technique removes such a

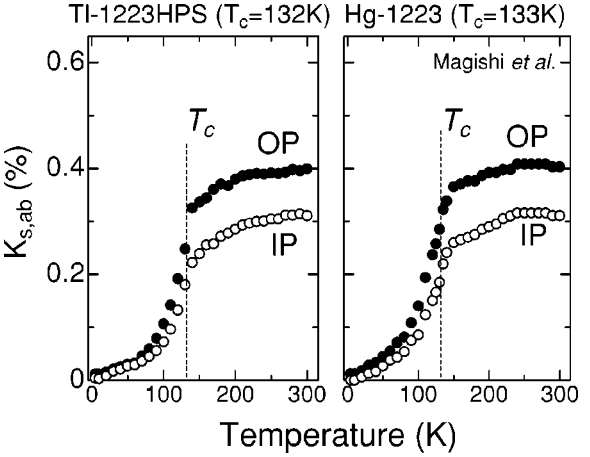

FIG. 1. T dependence of the spin part of Knight shift $K_{s,ab}(T)$ of ^{63}Cu for the c axis $\perp H$ in Tl-1223HPS-1 ($T_c = 132$ K) and Hg-1223 ($T_c = 133$ K). Both indicate a similar behavior at the IP and OP (see the text).

disorder where Tl is substituted for Ca, leading to the significant increase in T_c.

II. EXPERIMENTAL RESULTS AND DISCUSSION

Polycrystalline samples were prepared by the HPS technique as described elsewhere.[2] Two samples were used with nominal compositions, i.e., $Tl_{0.75}Ba_2Ca_2Cu_{3.25}O_{10-y}$ (Tl-1223HPS-I) and $TlBa_2Ca_2Cu_3O_{10-y}$ (Tl-1223HPS-II) that exhibit the SC transition at $T_c = 132$ K and 130 K, respectively. Energy dispersive x-ray spectroscopy measurement indicates that actual compositions of both the samples are almost stoichiometric.[2] T_c was determined at an onset temperature below which a diamagnetic signal appears in dc susceptibility. The powder samples were aligned along the c axis at an external magnetic field $H = 15.5$ T and fixed by the Stycast 1266 epoxy. The Tl- and Cu-NMR measurements were performed using a conventional phase-coherent-type NMR spectrometer. The Knight shift and T_1 of ^{63}Cu were measured at the central peak ($-1/2 \Leftrightarrow 1/2$ transition) in the NMR spectrum split by the electric quadrupole effect.

Figure 1 indicates the temperature (T) dependence of the spin part in ^{63}Cu Knight shift, $^{63}K_{s,ab}(T)$ at the IP and OP for the c axis $\perp H_0$ of Tl-1223HPS-I and Hg-1223. Note that the $^{63}K_{s,ab}(T)$'s in Tl-1223HPS-I and -II are independent of a starting nominal composition of constituents as far as T_c exceeds 130 K. The $K_{s,ab}(T)$ at the IP and OP that are proportional to the respective uniform susceptibilities $\chi_s(T)$, are related to N_h(IP) and N_h(OP) in multilayered high-T_c cuprates.[6] As the hole content N_h in a CuO_2 plane increases, the value of $K_{s,ab}$ increases at the normal state in most high-T_c cuprates. The fact that $K_{s,ab}$ at the OP is larger than that at the IP indicates that N_h(OP) is larger than N_h(IP). It is remarkable that the T dependence and the value of $K_{s,ab}(T)$ at room temperature in Tl-1223HPS-I coincides with those in Hg-1223. In other words, the N_h(IP) and N_h(OP) in Tl-1223HPS-I are almost the same as those in Hg-1223, which are in a nearly optimum doping level.

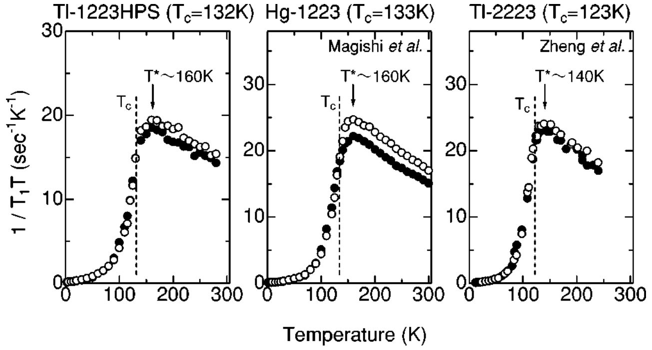

FIG. 2. T dependence of $1/T_1T$ in Tl-1223HPS-I ($T_c = 132$ K) and Hg-1223 ($T_c = 133$ K) along with the data for the annealed Tl-2223 ($T_c = 123$ K). In addition to the common increase in $1/T_1T$ upon cooling due to the AFM spin fluctuations, the pseudogap behavior is commonly seen below $T^* \sim 160$ K for Tl-1223HPS-I and Hg-1223 with the highest T_c to date.

In Fig. 2, the T dependences of $^{63}(1/T_1T)$ are presented for Tl-1223HPS-I, Hg-1223 (Ref. 7), and Tl-2223 (Ref. 8) with $T_c = 132$, 133, and 123 K, respectively. $^{63}(1/T_1T)$ increases with decreasing T due to the development of AFM spin fluctuations. The value of $1/T_1T$ at the IP is slightly larger than at the OP, since N_h(IP) is slightly smaller than N_h(OP). The similarity of magnetic properties is also seen in the pseudogap behavior where the $(1/T_1T)$'s in Tl-1223HPS-I and Hg-1223 reveal a maximum at $T^* = 160$ K for both the IP and OP. Evidently, the $^{63}K(T)$ and $^{63}(1/T_1T)$ results reveal that both the compounds have common magnetic characters.

Next, we argue the SC characteristics from the $1/T_1$ behavior. As indicated in Fig. 3, $1/T_1$ decreases just below T_c, followed by a typical behavior for most high-T_c compounds, consistent with the d-wave SC state with a line-node gap. It should be noted that a $T_1T = \text{const}$ behavior has been commonly observed far below T_c in most high-T_c compounds. For example, in the figure, the $1/T_1T$ data on $BiSr_2Ca_{0.95}Y_{0.05}Cu_2O_y$ (Bi-2212) and $YBa_2Cu_3O_7$ (Y-1237) are shown along with the data on Tl-1223HPS-I, Hg-1223, and Tl-2223. It was established that this behavior originates from the residual density of states $N_{res}(E_F)$ at the Fermi level and that $N_{res}(E_F)$ is induced by the crystal distortion and/or imperfection, or impurities. Even when T_c is not significantly suppressed, the appearance of $N_{res}(E_F)$ is characteristic for the unconventional superconductivity with the line-node gap. It is possible to estimate $N_{res}(E_F)$ following the relation of

$$\frac{N_{res}}{N_0} = \sqrt{\frac{(1/T_1T)_{low-T}}{(1/T_1T)_{T_c}}}, \tag{1}$$

noting that $1/T_1T$ is proportional to the square of the density of states in general. It is evident that a N_{res}/N_0 in Tl-1223HPS-I is smaller than in Tl-2223, comparable to the values of Hg-1223. Using the above relation, the respective values of N_{res}/N_0 at the IP and OP are evaluated to be 0.10 and 0.09 in Tl-1223HPS-I ($T_c = 132$ K) and 0.11 and 0.09 in Tl-1223HPS-II ($T_c = 130$ K). The value of N_{res}/N_0 is 0.19

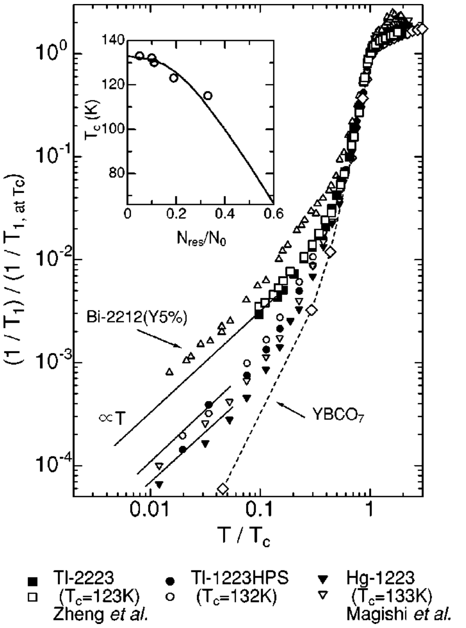

FIG. 3. T dependence of $1/T_1$ in the SC state for various high-T_c compounds. Here the solid (open) symbols correspond to the data at the OP (IP). The $1/T_1$ reveals a universal behavior just below T_c, followed by a T_1T=const behavior at low temperatures as marked by solid lines as a guide to the eye. Note that, in Y-1237 that is considered to be one of best quality samples among high-T_c cuprates, the T_1T=const behavior appears only at very low T as seen by the dashed line. Its values in Tl-1223HPS-I and Hg-1223 with the highest T_c to date are much smaller than those in the optimally doped Bi-2212 (T_c=94 K) and the annealed Tl-2223 (T_c=123 K). This gives evidence for a correlation between the value of T_c and the extent of any disorder that results in the increase of the residual density of state $N_{res}(E_F)$. The inset indicates $N_{res}(E_F)$ vs T_c where the solid curve is the theoretical calculation by Hotta in terms of a unitarity limit for impurity scattering. Even though some impurities are not explicitly introduced into the samples, some inhomogeneity in crystal structure such as crystal imperfection and/or defect cause impurity scattering to reduce T_c. The increase in T_c in Tl-1223HPS is because the substitution effect of Tl for Ca is removed (see text).

(0.18) at the IP (OP) in the annealed Tl-2223 with T_c=123 K (Ref. 9), and 0.33 (0.29) at the IP (OP) in the as-grown Tl-2223 with T_c=115 K (Ref. 8) should be noted. The inset in Fig. 3 shows T_c vs N_{res}/N_0 plots, where the solid curve is the calculation reported by Hotta in terms of the unitarity limit for impurity scattering,[10] being in good agreement with the experiment.

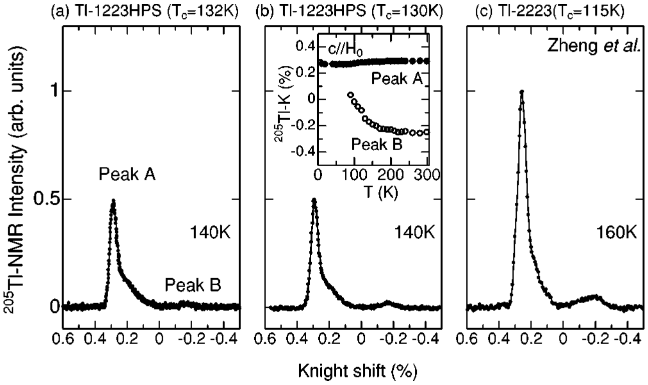

FIG. 4. ^{205}Tl spectra of Tl-1223HPS-I (T_c=132 K), Tl-1223HPS-II (T_c=130 K), and the as-grown Tl-2223 (T_c=115 K). A main peak at the A site at a low field arises from the Tl site in charge reservoir layer, whereas a satellite peak at the B site at a high field arises from the Tl site that is replaced into the Ca site. The substitution of Tl for Ca is decreased for the Tl-1223 that was synthesized at high pressures. A-site peaks are normalized per Tl site. The inset of Fig. 4(b) indicates the T dependence of Knight shifts at the A and B sites in Tl-1223HPS-II with T_c=130 K.

What is an origin of the pair-breaking effect in the Tl-1223 compounds? This was addressed from the Tl-NMR experiment. Figures 4(a) and 4(b) indicate Tl-NMR spectra for the c axis $\perp H_0$ in Tl-1223HPS-I and -II that were synthesized with a different nominal composition. Figure 4(c) indicates the spectrum in the as-grown Tl-2223 (T_c=115 K).[9] In Tl 2223, a main peak at a A site at a low field arose from the Tl sites in charge reservoir layers, whereas a satellite peak at a B site at a high field from minority Tl sites. The hyperfine field at the B site was shown to originate from the mixing between the Cu $3d$, O $2p$, Tl and $5d$ states, and hence the B site arises from the Tl sites that are substituted for the Ca sites.[8] As seen in the inset of Fig. 4(b), in the present compound the main peak is almost T independent with a small positive shift, whereas the satellite one reveals a negative large shift that is decreased in its absolute value below T_c, in agreement with that in Tl-2223. Hence, the B site in Tl-1223 is due to Tl that substituted the Ca site as well. This is also corroborated by other experiments.[2] It is evident that the intensity at the B site in Tl-1223HPS-I is smaller than that in Tl-2223. The respective intensity ratios of the B to A sites are estimated as 1.9% and 3.3% in Tl-1223HPS-I and -II that reveal T_c=132 and 130 K, whereas as 10.5% in Tl-2223 with T_c=115 K. The decrease in the content of Tl at the Ca layers is a main cause for the T_c enhancement. The decrease in the linewidth of Cu-NMR spectrum is correlated with the increase in T_c as well, as described in detail below.

In Table I are summarized the N_{res}/N_0's and the linewidths of Cu-NMR spectra at the IP and OP under the c axis

TABLE I. The N_{res}/N_0 and the linewidth of Cu-NMR spectra at the IP and OP under the c axis $\perp H_0$ are listed up for Tl-1223HPS-I (T_c=132 K), Hg-1223, and Bi-2212. The respective linewidths of Cu-NMR spectrum at the IP and OP in Tl-1223HPS-I are quite narrow compared with that of Tl-2223.

	T_c (K)		N_{res}	Linewidth (Oe)
Hg-1223 (Ref. 7)	133	IP	0.05	70
		OP	0.05	240
Tl-1223HPS	132	IP	0.10	90
		OP	0.09	150
Tl-2223 (Ref. 8)	123	IP	0.19	150
		OP	0.18	270
Bi-2212	94		0.23	~400

$\perp H_0$ in the Hg-1223, Tl-1223HPS-I ($T_c = 132$ K), Tl-2223, and Bi-2212. The respective linewidths of Cu-NMR spectrum at the IP and OP in Tl-1223HPS-I are narrower than that of the annealed Tl-2223, and especially, the IP width is close to Hg-1223. It was pointed out that the N_{res}/N_0 at the IP is larger than that at the OP in Tl-2223 (Ref. 8). This appears to be generic in all the Tl systems as we have shown in this study. We conclude that some crystal imperfection, which is introduced by the substitution of Tl for Ca, seems to map onto the CuO_2 plane so as to act as if the impurity scattering is in a regime of unitarity limit. The present experiment has clarified that the cause for the T_c enhancement in Tl-1223HPS is because the substitution of Tl for Ca is much more reduced than in Tl-2223 synthesized by a standard technique. The HPS technique is thus very efficient in reducing the extent of disorder and as a result raising T_c.

Finally, we comment on the inhomogeneity effect of SC and magnetic properties that are introduced by some crystal imperfection in an optimally doped Bi-2212 with $T_c = 94$ K. The scanning tunnel microscope (STM) study unraveled a local inhomogeneity in the local density of states and the SC gap in Bi-2212 system.[11] Pan *et al.* suggested that the inhomogeneity is a consequence of doping to a Mott insulator.[11] However, it was revealed from the Cu-NMR studies that Bi-2212 reveals a large value of $N_{res}/N_0 = 0.23$ and a quite broad linewidth of Cu-NMR spectrum, even though a single crystal is used. These results demonstrate that the extent of disorder at the CuO_2 plane is significantly larger than in other high-T_c compounds, and that such a disorder is not due to the Y doping, because such a disorder already exists in the undoped Bi-2212.[12] The inhomogeneity in Bi-2212 revealed by the Cu-NMR studies might be related with that from the STM study. The large inhomogeneity in Bi-2212 seems to be a special and unique problem inherent to this system. Therefore, we suggest that the inhomogeneous effect might not be necessarily common or inevitable in other high-T_c superconductors. The STM investigations are highly desired on other high-T_c systems that exhibit a smaller value of $N_{res}(E_F)$ and a narrower linewidth of the Cu-NMR spectrum in order to extract any intrinsic magnetic and SC properties in high-T_c cuprates.

III. CONCLUSION

In summary, the ^{63}Cu- and ^{205}Tl-NMR measurements have unraveled why a high value of $T_c > 130$ K was obtained in the trilayered high-T_c compounds $TlBa_2Ca_2Cu_3O_{10-y}$ that were synthesized at a high pressure. In the normal state, the Knight shift and T_1 revealed almost the same behaviors as those in Hg-1223 that exhibits the highest $T_c = 133$ K to date. In the SC state, the T dependence of $1/T_1$ decreased rapidly below T_c followed by a $T_1T = \text{const}$ behavior at very low T. The results are accounted for by the *d*-wave pairing model where the presence of the residual density of states $N_{res}(E_F)$ is incorporated at the Fermi level to be consistent with the experiments. The important finding is that the size in $N_{res}(E_F)$ is much smaller for Tl-1223HPS ($T_c = 132$ K and 130 K) than for Tl-2223 ($T_c = 123$ K and 115 K). Correspondingly, it is shown that an NMR intensity at a satellite peak in the Tl-NMR spectrum, which originates from a possible substitution of Tl for Ca, is much smaller for the former than for the latter. This demonstrates that as a result of decreasing the degree of any disorder effect, the T_c in Tl-1223 reveals a value higher than $T_c \sim 130$ K. The inevitable substitution of Tl for Ca may bring about some disorder that is mapped onto the CuO_2 plane, resulting in the appreciable suppression in T_c. The present work has demonstrated from a microscopic point of view that the synthesis technique at high pressures is a good way to remove such a crystal imperfection.

ACKNOWLEDGMENTS

We acknowledge helpful discussions with K. Magishi. This work was partly supported by the COE Research (10CE2004) in a Grant-in-Aid for scientific research from the Ministry of Education, Sports, Science, and Culture of Japan. One of the authors (Y. Tokunaga) was partially supported by JSPS.

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