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Pseudogap behavior in single-crystal $Bi_2Sr_2CaCu_2O_{8+\delta}$ probed by Cu NMR

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We report that the nuclear spin-lattice relaxation rate divided by temperature, $1/T_1T$, has a broad maximum around $T^* \sim 210$ K and ~ 100 K in underdoped and overdoped single crystals of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) with $T_c = 79$ and 77.3 K, respectively, showing the normal-state spin-gap behavior. One result is that the steep decrease in the ^{63}Cu Knight shift, $K(T)$, has been observed below $T^*_K \sim 200$ K and ~ 100 K, suggesting the normal-state pseudogap behavior in quasiparticle density of states (DOS), which is consistent with the pseudogap behavior below $T^*_{\rm ARPES} \sim 170$ K revealed on underdoped Bi2212 from studies of angle-resolved photoemission spectroscopy. We propose that the spin-gap behavior in $1/T_1T$ has the same origin as the pseudogap in the quasiparticle DOS. [S0163-1829(98)51534-2]

In underdoped cuprates, there is considerable evidence that the pseudogap in the magnetic and electronic excitation spectra is already formed in the normal state above T_c. From studies of the magnetic excitation spectrum,[1–5] the spin-gap behavior was first reported and the pseudogap in the electronic excitation spectrum later from a variety of other probes.[6–11] Recent studies by Ding *et al.* and Harris *et al.* of angle-resolved photoemission spectroscopy (ARPES) in underdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) revealed that the pseudogap with d-wave symmetry opens below $T^*_{\rm ARPES} \sim 170$ K and 225 K, respectively, and these authors suggested that the pseudogap develops into the d-wave superconducting gap once phase coherence is established below T_c.[7–9] The result was interpreted as evidence in favor of a preformed d-wave gap. The $T^*_{\rm ARPES}$ seems to increase above ~ 300 K in the underdoped Bi2212 with $T_c = 10$ K.[7]

It was reported on underdoped $YBa_2Cu_3O_{6.6}$ ($YBCO_{6.6}$) that the Knight shift $K(T)$ decreases upon cooling from $T_{\rm mK}$,[4] whereas the spin-lattice relaxation rate divided by temperature, $1/T_1T$, has a broad maximum around $T^* \sim 150$ K far above T_c but below $T_{\rm mK}$.[1–3] Recently, this behavior was also found in underdoped Hg-based compounds with mono- and three CuO_2 layers.[12–14] The anomalous suppression in the spectral weight of the low-energy spin dynamics below T^* is referred to as a *spin-gap* behavior[1] and was confirmed by subsequent neutron experiments.[5] However, the $1/T_1T$ in underdoped $La_{2-x}Sr_xCuO_4$ (LSCO) (Ref. 15) does not show the spin-gap behavior, but increases continuously close to T_c, whereas the spin susceptibility deduced from the $K(T)$ in underdoped LSCO undergoes a continuous decrease below $T_{\rm mK}$.[15–17] On the other hand, Loram *et al.* suggested from susceptibility and high-resolution specific heat measurements that *pseudogap* is developed below $T_{\rm mK}$ upon cooling in the normal-state quasiparticle spectrum.[18] The anomalies around T_m are also shown from measurements of Hall coefficients and thermoelectric power in LSCO.[19] There is as yet no general consensus on a consistent interpretation of these magnetic anomalies related to the Knight shift and $1/T_1T$.

Even in the NMR community, there is no consensus about this issue. As a matter of fact, Yasuoka *et al.* insisted that the decrease in $1/T_1T$ below T^* is ascribed to an opening of a pseudogap in the antiferromagnetic (AF) spin excitation spectrum, and estimated from the rapid decrease in $1/T_1T$ between T_c and T^* that an *activated-gap* size, Δ_{T_1}, is in a range of 13–18 meV for various underdoped compounds.[20] Although they stressed that this spin gap should not be directly related to the superconducting gap, they considered that the appearance of the spin gap is likely to be related to the mechanism of high-T_c superconductivity. On the other hand, Williams *et al.* claimed that the reduction in Knight shift from $T_{\rm mK}$ is due to the presence of a pseudogap with the *d-wave symmetry* in the quasiparticle density of states (DOS) in the normal state.[21] They analyzed the decreasing behavior of $K(T)$ over the entire temperature range by assuming a gap comprising the pseudogap (E_g) and the superconducting gap (Δ_s), $\Delta^2 = \Delta_s^2 + E_g^2$ and claimed that since E_g scales to a maximum value of T_c in various cuprates, the pseudogap and the superconducting gap have a similar energy scale. In their analyses, however, the spin-gap behavior in $1/T_1T$ was ignored completely. In addition, Bobroff *et al.* claimed from the ^{17}O Knight shift, $^{17}K(T)$ measurement on underdoped $HgBa_2CuO_{4+\delta}$ that $^{17}K(T)$ extrapolates to zero at $T > 0$, which indicates the opening of a pseudogap at $T^* > T_c$.[12] They considered that the pseudogap temperature T^* may be defined as a crossover temperature between the decreasing behavior and the flat high temperature part in $^{17}K(T)$. The different temperature dependence of $1/T_1T$ and $K(T)$ has never been interpreted in a consistent manner on a same footing.

Since ARPES,[7–9] tunneling spectroscopy,[22,23] and thermal and transport measurements[24] are being carried out on Bi2212 single crystals where the doping level varies from underdoping to overdoping, it is important to compare the pseudogap behavior probed from various experimental techniques with those evidenced from the T_1 and the Knight shift data. In this paper, we report Cu-NMR measurements in underdoped and overdoped Bi2212 single crystals with $T_c \sim 79$ and 77.3 K, respectively. In the underdoped Bi2212, a broad peak in $1/T_1T$ is observed at $T^* \sim 210$ K and the steep decrease in $K(T)$ occurs below $T_K^* \sim 200$ K, deviating from a T-linear-like gradual decrease below a much higher temperature, $T_{\rm mK}$. It is pointed out that the latter result is consistent with the ARPES results that the gap opens below $T^*_{\rm ARPES} \sim 170$ K reported by Ding *et al.*[7] and 225 K by Harris *et al.*[9] for samples with almost the same doping level. The remarkable coincidence among these gaplike features leads us to the conclusion that the spin-gap behavior in $1/T_1T$ has the same origin as the pseudogap in the quasiparticle DOS evidenced from the Knight shift and the ARPES results. Furthermore, we suggest that the overdoped Bi2212 also reveals the pseudogap behavior around $T^* \sim T_K^* \sim 100$ K close to $T_c = 77$ K. The present NMR studies on the Bi2212 single crystals have provided detailed information about the nature of the pseudogap not only in the collective AF-spin excitation spectrum but also in the quasiparticle DOS.

Single crystals of Bi2212 were synthesized by the floating zone method. Underdoped ($T_c = 79$ K) and overdoped ($T_c = 77.3$ K) single crystals were prepared by annealing at 600 °C under $P(O_2) = 4.67 \times 10^{-4}$ atm for one day at 400 °C and under $P(O_2) = 2.1$ atm for three days, respectively. The temperature width in the superconducting transition is about 3 K for both samples. The superconducting fraction in the underdoped and overdoped samples is nearly the same, since the size of the diamagnetic shielding signal for each is comparable. From the dependence of T_c on carrier-hole concentration p per the CuO_2 plane,[25] p in the underdoped and overdoped samples is estimated to be ~ 0.125 and ~ 0.225, respectively. Cu NMR measurements were performed at the frequency of 178.1 MHz using a 16 T (4.2 K) superconducting magnet. The nuclear spin-lattice relaxation time T_1 was measured by the saturation recovery method. Above 40 K, a single component of T_1 was determined by fitting the recovery of the nuclear magnetization $M(t)$ after saturation pulses to the theoretical relaxation function $[M(\infty) - M(t)]/M(t) = 0.1\exp(-t/T_1) + 0.9\exp(-6t/T_1)$. To investigate an evolution of magnetic behavior with respect to hole content, we include the previous results of the $1/T_1T$ and the Knight shift in optimally doped Bi2212 ($T_c \sim 86$ K, $p \sim 0.20$.)[26,27] NMR data in overdoped Bi2212 ($T_c = 77$ K) have already been reported by Walstedt *et al.*[28] The present NMR results in the overdoped Bi2212 are found to be consistent with their results.

Figure 1 shows the T dependence of the Knight shift parallel to the c axis, $K_c(T)$ in the underdoped and overdoped Bi2212. The K_c in the underdoped Bi2212 decreases linearly in the range 200 K−300 K, whereas it undergoes a marked decrease below $T_K^* \sim 200$ K, exhibiting a small anomaly at T_c. In contrast, the K_c in the overdoped Bi2212 decreases gradually below ~ 100 K from a constant value in temperatures higher than 100 K and steeply below $T_c = 77.3$ K. The K_c at 4.2 K consists of the orbital contribution from the $3d_{x^2-y^2}$ orbit, the superconducting diamagnetic contribution and the spin shift originating from the residual density of states (RDOS) in the superconducting state. The presence of RDOS was verified from the observation of $T_1T =$ constant behavior at low temperatures.[26] By subtracting such T-independent contributions from the measured Knight shift data $K_{\rm obs}$, the T-dependent part of the Knight shift $\Delta K(T) = K_{\rm obs} - K(4.2\text{ K})$ is shown in Fig. 2, together with the data in the optimally doped Bi2212 reported previously.[26,27] In the optimally doped Bi2212, since the accuracy of the ^{63}Cu Knight shift is poor, the $\Delta^{17}K(T)$ deduced from the ^{17}O Knight shift data reported by Takigawa and Mitzi are also plotted for comparison.[27] For each compound, the decreasing behavior in $\Delta K(T)$ is different, reflecting their different doping level.

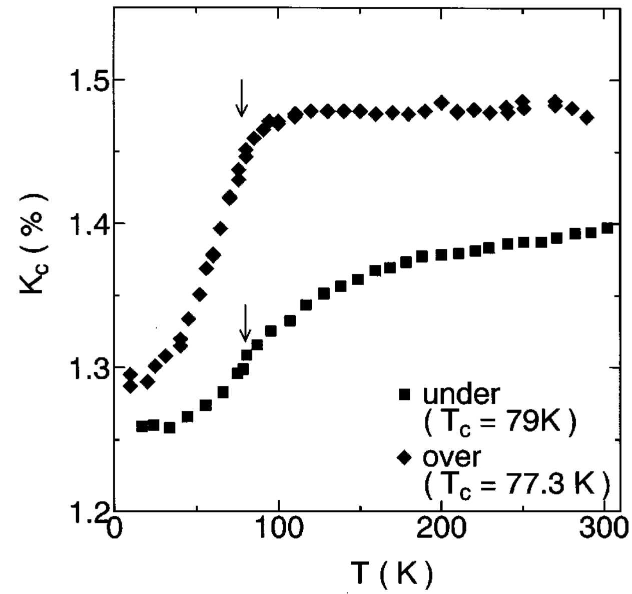

FIG. 1. T dependence of the Knight shift parallel to the c axis (K_c) in underdoped and overdoped Bi2212. Arrow indicates T_c for each compound.

In order to characterize the respective T variation in $\Delta K(T)$ upon cooling, we plot in Fig. 3 the temperature-derivative change in $\Delta K(T)$, $dK(T)/dT$ as a function of temperature. From the respective behavior for the underdoped and optimally doped Bi2212 in Fig. 3, two character-

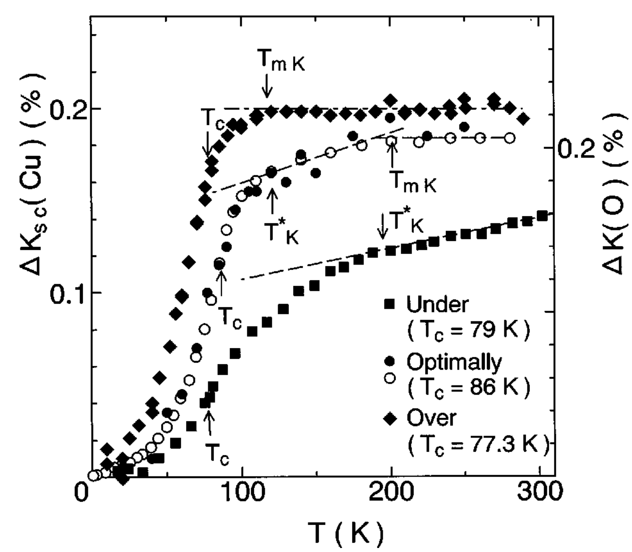

FIG. 2. T-dependent spin part K_{cs}(Cu) in K_c in underdoped, optimally doped, and overdoped Bi2212. The T-dependent spin part K_s(O) in the ^{17}O Knight shift in optimally doped Bi2212 reported by Takigawa *et al.* is also plotted by open circles (Ref. 27). The anomalies at T_c, T_K^*, and $T_{\rm mK}$ are indicated by arrows (see text).

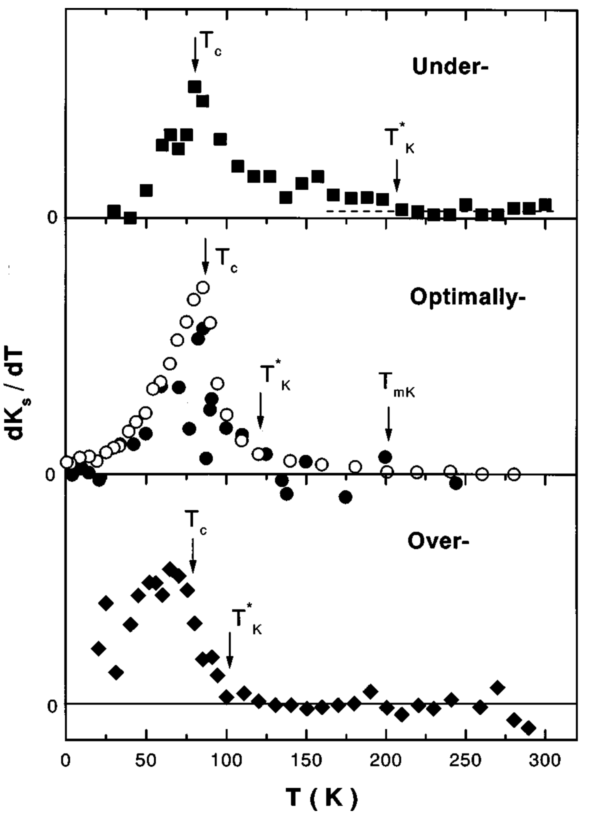

FIG. 3. T dependence of T derivatives of the spin part in ^{63}Cu Knight shift for (a) underdoped, (b) optimally doped, and (c) overdoped Bi2212. Open circles in (b) are the T derivatives in the ^{17}O Knight shift reported by Takigawa (Ref. 27). Arrows show the anomalies at T_c, T^*_K, and T_{mK}.

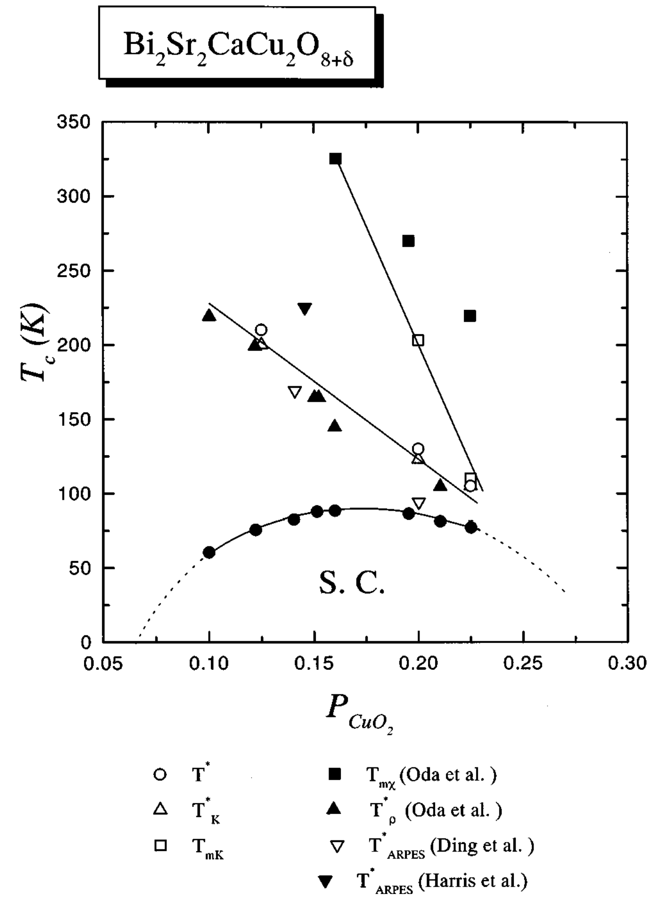

FIG. 5. Hole content p dependence of characteristic temperatures below which an anomaly appears in various measurements (see text).

istic temperatures of T_{mK} and T^*_K are defined as the temperatures where $dK(T)/dT$ begins to increase from zero and increase steeply from a finite value, respectively. In the optimally doped Bi2212, $T_{mK}\sim 203$ K and $T^*_K\sim 123$ K are deduced. In the underdoped Bi2212, T_{mK} shifts to a temperature higher than room temperature and $T^*_K\sim 200$ K. By contrast, T^*_K and T_{mK} in the overdoped Bi2212 cannot be exactly distinguished from one another as seen in Fig. 3.

We turn to the nuclear-relaxation behavior in both the samples. Figure 4 shows the T dependence of $1/T_1T$ in the underdoped and overdoped Bi2212 together with the data in the optimally doped Bi2212.[26] The $1/T_1T$ in the underdoped Bi2212 reveals a broad maximum around $T^*\sim 210$ K and continues to decrease without any clear change at T_c. The value of $1/T_1T$ at T_c has decreased to 34% of its value at T^*, which is lower than the underdoped $YBa_2Cu_3O_{6.6}$ (63%) (Ref. 3) and $YBa_2Cu_4O_8$ (57%),[29] and is comparable with that in the underdoped $HgBa_2CuO_{4+\delta}$ with $T_c=80$ K (27%).[13] In the optimally doped and the overdoped Bi2212, T^* is reduced to $\sim$130 K and $\sim$100 K, respectively. In contrast to the underdoped Bi2212, the steep decrease in $1/T_1T$ is clear below T_c for both the samples. A striking result is that T^* is close to T^*_K for the underdoped and optimally doped Bi2212. Even in the overdoped Bi2212, T^* is close to $T_{mK}\sim T^*_K$. These results provide evidence that the spin-gap behavior in $1/T_1T$ below T^* has the same origin as the pseudogap behavior in the quasiparticle DOS below T^*_K.

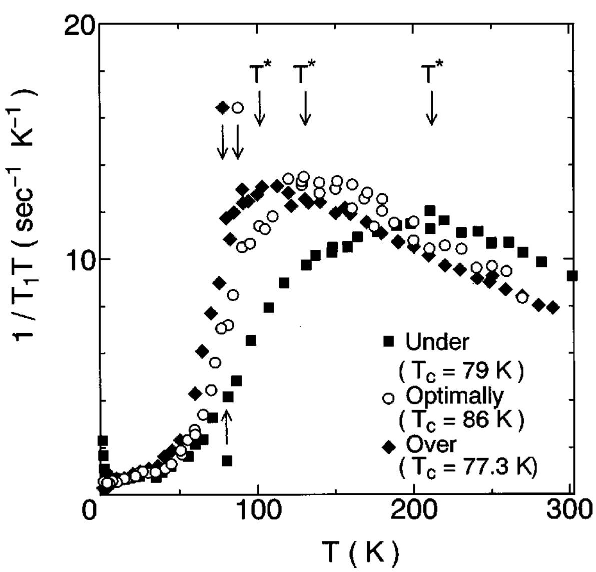

FIG. 4. T dependence of $1/T_1T$ in underdoped, optimally doped, and overdoped Bi2212. Arrows indicate T_c and T^* for each compound.

Next we discuss the gradual decrease in $\Delta K(T)$ as temperature decreases from T_{mK} to T^*. Since $1/T_1T$ continues to increase between T_{mK} and T^* where $\Delta K(T)$ decreases gradually as seen in Figs. 2 and 4, the likely cause for the gradual decrease in $K(T)$ is associated with the development of AF-spin correlations towards T^*, which is also suggested from the recent theoretical studies.[30,31] In the gapless quantum-spin systems such as one dimensional $S=1/2$ linear spin-chain Sr_2CuO_3 (Ref. 32) and three-leg spin-ladder $Sr_3Cu_2O_5$,[33] the gradual decrease in susceptibility was observed as temperature decreases. This means that the gradual decrease in static susceptibility in the underdoped and optimally doped Bi2212 is not always related with the opening of the pseudogap. Rather, the sharp decrease in $^{63}K(T)$ below T_K^*, where $1/T_1T$ starts to decrease, should be ascribed to the opening of the pseudogap. We note that an extrapolation of pronounced decrease in $\Delta K(T)$ in the normal state near T_c intercepts to the temperature axis at $T>0$ in the $\Delta K(T)$ vs T plot in Fig. 2. This feature is consistent with the ^{17}O Knight shift data in underdoped $HgBa_2CuO_{4+\delta}$ single-layer cuprates.[12]

To summarize the present NMR results, we present in Fig. 5 the hole content dependence of T^*, T_K^*, and T_{mK} together with various characteristic temperatures at which an anomaly was observed by other experimental probes. Oda *et al.* reported that the in-plane resistivity starts to deviate downward from a T-linear-like behavior below T_ρ^* and that the uniform susceptibility $\chi(T)$ starts to decrease gradually below $T_{m\chi}$.[24] As seen in Fig. 5, it is obvious that $T^* \sim T_K^* \sim T_\rho^* \sim T_{\mathrm{ARPES}}^*$, which increase with decreasing hole content. This agreement in various characteristic temperatures suggests strongly that the pseudogap opens not only in the AF-spin excitation spectrum at low energy around $\mathbf{Q}=(\pi,\pi)$ but also in the quasiparticle DOS. Furthermore, the tunneling spectroscopy on the same optimally doped Bi2212 reveals that the normal-state pseudogap opens in the quasiparticle DOS around 120 K close to $T^* \sim$ 130 K.[23] Convincing evidence is increasing to indicate that the pseudogap in the quasiparticle DOS and the spin gap observed in $1/T_1T$ has the same origin in a series of Bi2212 single crystals where the doping level varies from underdoping to overdoping. By contrast, other characteristic temperatures, T_{mK} and $T_{m\chi}$, below which the Knight shift and the susceptibility decrease gradually, respectively, have nothing to do with the pseudogap formation, but provide a signature for the development of AF-spin correlations.

It is still a key issue whether the pseudogap is associated with a *spin gap* signaling a non-Fermi-liquid state based on a concept of a spin-charge separation,[34] or a normal-state precursor of the d-wave superconducting gap[35] or a precursor to a spin density wave state.[30,36] At the present stage, we cannot determine an origin of the pseudogap. However, we suggest from the present NMR result that the pseudogap and the superconducting gap are the same in origin, since the anomaly of $1/T_1T$ in the underdoped Bi2212 is not observed at T_c.

In order to settle the above issue, it is important to inspect whether T^*, T_K^*, and T_{ARPES}^* continue to increase when the holes are decreased near the superconducting to nonmetallic and magnetic phase boundaries. To check this, we remark that further systematic experiments are planned on the same Bi-based single crystals.

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