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Nuclear spin-lattice relaxation and antiferromagnetic spin correlations in superconducting thiospinel $\mathrm{Cu_{1.5}Co_{1.5}S_4}$

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The antiferromagnetic and superconducting properties of a thiospinel $\mathrm{Cu_{1.5}Co_{1.5}S_4}$ ($T_N = 19.0$ K, $T_c = 2.3$ K) have been investigated with ^{63}Cu NMR (75 MHz), ^{59}Co NMR (75 MHz), and ^{59}Co pure quadrupole resonance between $T = 1.23$ and 150 K. The linear dependence of negative ^{63}Cu Knight shift (-0.013% at 4.2 K) on the Curie-Weiss-type susceptibility $\chi(T)$ and nearly independent ^{59}Co Knight shift ($+1.43\%$) indicate that the d hole band of Cu at the tetrahedral A site is mainly responsible for the spin paramagnetism. The spin-lattice relaxation rates $(T_1T)^{-1}$ of both ^{63}Cu and ^{59}Co are significantly enhanced with lowering temperature below ~ 100 K, similar to those observed in high-T_c copper oxygen perovskite superconductors, which are associated with the growth of antiferromagntic spin correlations at low temperatures. Below T_c, T_1^{-1} of the fractional Co at the octahedral B site, which increases from $\sim 0\%$ at $0.65T_c$ to $\sim 30\%$ at $0.5T_c$, shows a rapid decrease, indicating a partial formation of the superconducting energy gap. On the other hand, T_1^{-1} of the dominant part of Co follows a Korringa-like relation down to $0.5T_c$, suggesting it is in a gapless superconducting state, probably due to strong antiferromagnetic spin correlations.

Introduction. The possible incidence of magnetism, particularly the role played by antiferromagnetic (AF) spin fluctuations, on superconductivity and on normal-state properties has received wide interest in the study of the high-T_c copper oxygen perovskite superconductors (HTSC). In AF insulators, the configuration of $\mathrm{Cu^{2+}}$ ions in the $\mathrm{CuO_2}$ layers is $3d^9$ ($S = \frac{1}{2}$) and the ground state is well described by two-dimensional (2D) Heisenberg model.[1] By hole doping into the $\mathrm{CuO_2}$ planes, long-range AF order is destroyed and the system translates into a superconducting (SC) state.[2] Our current interest is focused on the experimental analysis of the proximity of the AF and SC phase.

On the other hand, extensive work on SC material research for copper sulfides has been done and, recently, Miyatani, Ishikawa, and Tanaka[3] found that most of the copper sulfide spinels and stannites, in which the Cu atoms are in the $\mathrm{Cu^{2+}}$ ($3d^9$) ionic state, show SC or superconductorlike behavior. They suggested that the origin of the observed SC can be attributed to the Cu-S bonds or to Cu-S defects similar to the case of Cu-O bonds in HTSC. Among the copper chalcogenide spinels, $\mathrm{Cu_{1+x}Co_{2-x}S_4}$ (Ref. 4) is interesting because it has a Curie-Weiss-type susceptibility with an AF behavior below T_N; this is shown in Fig. 1(a) and a SC transition at the lower temperature T_c, which largely depends on x, as the temperature dependence of the electrical resistivity is shown in Fig. 1(b).

In the case of the stoichiometric spinel $\mathrm{CuCo_2S_4}$ ($x = 0$), an x-ray-diffraction (XRD) intensity analysis suggests that it is a normal spinel. The Cu and Co atoms occupy the tetrahedral A site and the octahedral B site, respectively, and the ionic distribution is given by $\mathrm{Cu^{2+}[Co_2^{3+}]S_4}$. From temperature dependence of the magnetic susceptibility $\chi(T)$, the effective Bohr magneton μ_{eff} was estimated to be 0.985 μ_B/Cu. Taking the metallic p-type conductivity into consideration,[5] the $\mathrm{Cu^{2+}}(3d^9)$-S bonds provide the $3d$ hole band like the case of HTSC. The $\mathrm{Co^{3+}}$ ($3d^6$) ions take a low spin configuration ($S = 0$) as is explained from the NMR studies of Co in $\mathrm{Co_3S_4}$.[6,7]

In the case of $\mathrm{Cu_{1.5}Co_{1.5}S_4}$ ($x = 0.5$), the effect of additional Cu atoms is believed, from the XRD analysis, to substitute for the Co atos at the B site, and the ionic distribution is given by $\mathrm{Cu^{2+}[Cu_{0.5}^{2+}Co_{1.5}^{3+}]S_{4-\delta}}$. The Curie-Weiss-type susceptibility becomes more pronounced, as is shown in Fig. 1(a), and T_N increases from 17.5 K for $x = 0$ to 19.0 K for $x = 0.5$. A measurement of resistivity showed a SC transition at a low temperature, which took zero resistivity at $T_c = 2.3$ K, as is shown in Fig. 1(b). The electrical resistivity in the normal state obeys the quadratic law $\rho(T) = \rho_0 + AT^2$ at low temperatures,[8] suggesting that strong electron correlations or spin correlations play an important role in the normal state. Thus, we expect a possible coexistence of a prominent antiferromagnetism and superconductivity in the present thiospinel $\mathrm{Cu_{1.5}Co_{1.5}S_4}$.

In this paper, we report briefly the results of a nuclear-magnetic-resonance (NMR) study of ^{63}Cu and ^{59}Co and a pure-quadrupole-resonance (PQR) study of ^{59}Co in a poly-

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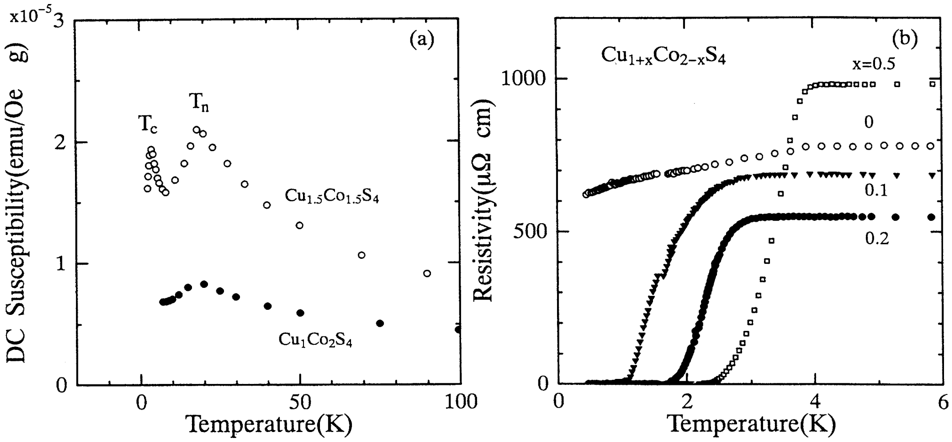

FIG. 1. Temperature dependencies of the susceptibility (a) and of the resistivity (b) of Cu$_{1-x}$Co$_{2-x}$S$_4$ ($x=0-0.5$) reported by Miyatani *et al.* (Ref. 4).

crystalline specimen of Cu$_{1.5}$Co$_{1.5}$S$_4$. The NMR has been known to be a useful tool for microscopic investigations of the magnetic and SC properties of HTSC,[9,10] in which AF correlations in the normal state were inferred from the large enhancement of the nuclear magnetic relaxation rate $(T_1T)^{-1}$ observed at Cu sites. The symmetry of the SC wave function was inferred from the T-dependence of T_1 in the SC state.[11]

Present experimental T_1 data of both ^{63}Cu and ^{59}Co also show the existence of significant $(T_1T)^{-1}$ enhancements in the normal state near T_c. The T_1 data of ^{59}Co in the SC state measured by PQR under a zero external magnetic field show a partial formation of the SC gap at the B sites. The T dependence of T_1, however, is not simply explained within the framework of the conventional BCS model, nor is it an analogy of T_1^{-1} behavior commonly observed in HTSC.

Experiment. The polycrystalline specimen of Cu$_{1.5}$Co$_{1.5}$S$_4$ [T_c(onset)=4.0 K, $T_c(\rho=0)=2.3$ K, $T_N=19.0$ K] used in the present resonance study was synthesized by a standard vacuum shielded ampoule method. The XRD measurements gave the lattice constant $a=9.470$ Å and u parameter 0.390. The magnetization measurement showed that the Meissner effect begins below T_c(onset)=4.0 K and presents ~100% diamagnetism at ~2.8 K.[4] The value of H_{C1} and H_{C2} at 1.4 K was ~0.10 kOe and ~10 kOe, respectively.

The NMR and PQR experiments were carried out using a phase-coherent spin-echo spectrometer operating at 75 and 5–7 MHz, respectively. Displayed in Figs. 2(a) and 2(b) are NMR spectra of ^{59}Co and ^{63}Cu in Cu$_{1.5}$Co$_{1.5}$S$_4$ obtained at 4.2 K and 75 MHz in a field sweeping procedure. PQR spectra were also observed around 5.6 MHz in a zero magnetic field. Figure 2(c) shows ^{59}Co PQR spectrum obtained at 4.2 K.

The NMR spectrum of ^{59}Co ($I=\frac{7}{2}$) shows a typical quadrupolar powder pattern attributed to the local trigonal symmetry at the octahedral B site. The value of the ^{59}Co Knight shift, K^{59}, and the quadrupole frequency, $\nu_Q^{59}=e^2qQ/14h$, deduced from the spectrum is +1.43% and 1.86 MHz, respectively, and they hardly depend on T in the measured range of 4.2–150 K within our experimental uncertainty. In the case of the PQR spectrum, the main resonance line at 5.6 MHz can be assigned to the $|\pm\frac{7}{2}\rangle \leftrightarrow |\pm\frac{5}{2}\rangle$ transition ($3\nu_Q$) of the ^{59}Co spin levels at the B site. A weak ^{59}Co resonance signal [hereafter labeled Co(II)], both in the PQR (at 6.3 MHz) and in the NMR ($K=1.92\%$, $\nu_Q=2.10$ MHz), was also observed. This spurious ^{59}Co(II) signal depends on the sample preparation procedures and reaches minimal (<10%) intensity for a specimen with the highest $T_c(x=0.5)$ and maximum Meissner fraction (~100%).

The NMR spectrum of ^{63}Cu ($I=\frac{3}{2}$) shown in Fig. 2(b) indicates a superposed structure with a sharp strong main line and a broad weak line. The main line lacks the quadrupole structure. Most of the observed ^{63}Cu signal is then attributed to the Cu atoms at the A sites, which have a local cubic symmetry. The broad and weak resonance line would be attributed to the quadrupolar broadened spectrum of the ^{63}Cu atoms in the octahedral B site with the local trigonal symmetry.

The Knight shift of ^{63}Cu, K^{63}, shows a slight temperature dependence as shown in Fig. 3, and takes a negative sign at low T (<25 K). The negative sign of K^{63} is indicative of a dominant d core-polarization hyperfine coupling between the nuclear and electron spins. These results of both K^{59} and K^{63} in Cu$_{1.5}$Co$_{1.5}$S$_4$ are close to those in CuCo$_2$S$_4$ as ob-

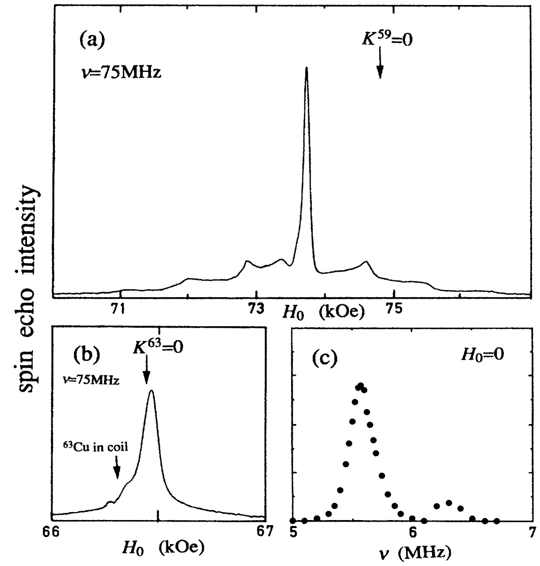

FIG. 2. Nuclear resonance spectra in Cu$_{1.5}$Co$_{1.5}$S$_4$ observed at 4.2 K: (a) ^{59}Co NMR spectrum at $\nu=75$ MHz; (b) ^{63}Cu NMR spectrum at $\nu=75$ MHz; (c) ^{59}Co PQR spectrum.

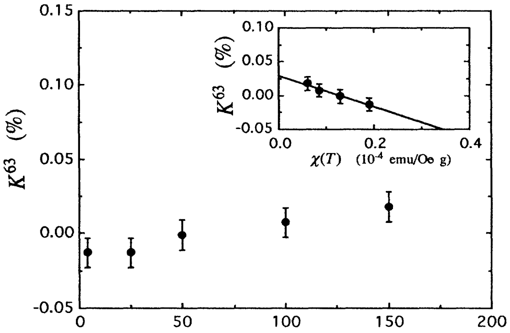

FIG. 3. Temperature dependence of K^{63} in $Cu_{1.5}Co_{1.5}S_4$. $K^{63}(T)$ vs $\chi(T)$ plot is shown in the inset.

tained by the cw NMR measurement by Locher.[6] From the $K^{63}(T)$ vs $\chi(T)$ plot shown in the inset of Fig. 3, the d-spin hyperfine coupling constant $A^{63}_{\rm hf}(d)$ for the Cu atoms at the A site is estimated to be -0.40 ± 0.1 kOe/μ_B, using the following relation:

$$A^{63}_{\rm hf}(d)=N\mu_B\, dK^{63}(T)/d\chi(T)\ , \qquad (1)$$

where N is the number of the Cu atoms at the A site per gram.

The spin-lattice relaxation time T_1 was measured utilizing the single-rf-pulse-saturation method. The magnetization recovery at the time t, $M(t)$, after the saturation-rf-comb-pulses is given by[12,13]

$$[M(\infty)-M(t)]/M(\infty)=a_1e^{-b_1t/T_1}+a_2^{-b_2t/T_1}$$
$$+a_3e^{-b_3t/T_1}+a_4e^{-b_4t/T_1}, \qquad (2)$$

where the coefficients b_i depend on the observed transition levels, and a_i on the initial saturation condition imposed on all the spin levels. In the present initial condition of single $\pi/2$ saturation pulse, b_i and a_i are given by $b_1=1$, $b_2=6$, $b_3=0$, $b_4=0$; $a_1=0.1$, $a_1=0.9$, $a_3=0$, $a_4=0$ for central $|\tfrac{1}{2}\rangle\leftrightarrow|-\tfrac{1}{2}\rangle$ transition of Cu NMR, $b_1=1$, $b_2=6$, $b_3=15$, $b_4=28$; $a_1=0.013$, $a_2=0.068$, $a_3=0.206$, $a_4=0.714$ for central $|\tfrac{1}{2}\rangle\leftrightarrow|-\tfrac{1}{2}\rangle$ transition of Co NMR and $b_1=3$, $b_2=10$, $b_3=21$, $b_4=0$; $a_1=0.214$, $a_2=0.649$, $a_3=0.136$, $a_4=0$ for $|\pm\tfrac{7}{2}\rangle\leftrightarrow|\pm\tfrac{5}{2}\rangle$ transition of Co PQR, respectively.

The experimental recovery data of both ^{63}Cu and ^{59}Co NMR, however, could not be reproduced by Eq. (2) with a corresponding set of coefficients. It is tentatively assumed, to explain the recovery, that the observed magnetization $M(t)$ is composed of two components: M_f with fast relaxation rate $T^{-1}_{1(f)}$ and M_s with slow rates $T^{-1}_{1(s)}$. We obtained a satisfactory fit with the following equation:

$$\frac{[M(\infty)-M(t)]}{M(\infty)}=M_f\sum_i a_ie^{-b_it/T_{1(f)}}+M_s\sum_i a_ie^{-b_it/T_{1(s)}}, \qquad (3)$$

where $M_f+M_s=1$. The M_f corresponding to the fraction with the fast relaxation rate $T^{-1}_{1(f)}$ was estimated to be ~70% for ^{63}Cu and ~90% for ^{59}Co from the NMR recovery data. The residual M_s fraction (~30%) of ^{63}Cu would be attributed to the Cu atoms at the B site with the slow rate $T^{-1}_{1(s)}$, in agreement with the above discussion about the spectrum structure. While the origin of the residual fraction M_s (~10%) of ^{59}Co which attributes to Co(II) is not understood yet, a probable explanation may be given by the induced anion defects. In the case of ^{59}Co PQR, on the other hand, the recovery behavior in the normal state ($T>T_c$) is sufficiently reproduced by Eq. (2). This is consistent with the fact that, in the case of the PQR spectra, the main ^{59}Co resonance line well separates from that of the spurious ^{59}Co(II), as shown in Fig. 2(c).

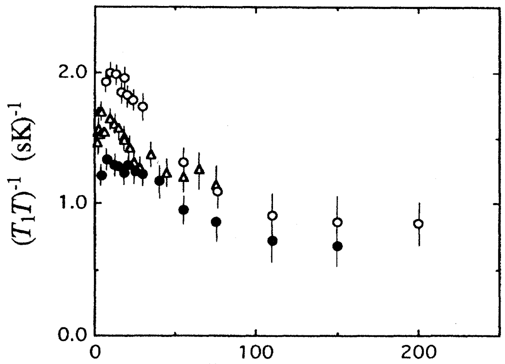

FIG. 4. Temperature dependencies of the relaxation rate in the normal state: ●, $(T_{1(f)}T)^{-1}$ of ^{63}Cu NMR; ○, $(T_{1(f)}T)^{-1}$ of ^{59}Co NMR; Δ, $(T_1T)^{-1}$ of ^{59}Co PQR.

Shown in Fig. 4 is the T dependencies of $(T_{1(f)}T)^{-1}$ of ^{63}Cu (solid circle) and ^{59}Co (open circle) measured at 66.5 kOe and 73.7 kOe, respectively, in the T range of 4.2–150 K. $(T_{1(f)}T)^{-1}$, of both ^{63}Cu originating from the A site and ^{59}Co from the B site, is significantly enhanced with lowering T below ~100 K. The T-dependencies of $(T_{1(s)}T)^{-1}$ of both ^{63}Cu and ^{59}Co are nearly the same with those of $(T_{1(f)}T)^{-1}$. The fact that $(T_{1(s)}T)^{-1}$ of ^{63}Cu is about one-third of $(T_{1(f)}T)^{-1}$ suggests that the Cu atoms substituted at the B site are in a nearly nonmagnetic state. The open triangle in Fig. 4 denotes $(T_1T)^{-1}$ of ^{59}Co deduced from the PQR measurement at 5.6 MHz under a zero magnetic field. In the normal state, $(T_1T)^{-1}$ at 0 kOe is also enhanced at low T, though the extent of the enhancement is smaller than that observed by NMR. The constant $(T_1T)^{-1}$ behavior above ~100 K is considered to be due to the dominant Van Vleck's d orbital contribution at high T.

The T dependence of T_1 below T_c was examined in detail by the ^{59}Co PQR. The recovery behavior of the magnetization after the $\pi/2$-saturation pulse could be reproduced by Eq. (2) with the single relaxation rate down to 1.5 K. However, as T was further lowered, a fractional component with slow relaxation rates was found to exist and grow. Then we utilized Eq. (3) to analyze the recovery data. The T-dependencies of $T_{1(f)}$ and $T_{1(s)}$, deduced through this procedure, are plotted in Fig. 5 by solid and open circles, respectively. The inset of Fig. 5 displays the T dependence of M_s with a slow relaxation rate, which increases from ~0% at 1.5 K to ~30% at 1.23 K. $T^{-1}_{1(s)}$, of the fractional component M_s of Co at the B site, shows an abrupt decrease below ~1.5 K, indicative of a partial formation of the SC energy gap. On the other hand, $T^{-1}_{1(f)}$ of the component M_f of Co follows roughly the Korringa-like relation $(T_1T)^{-1}\simeq1.5$ (sK)$^{-1}$ down to 1.23 K.

Discussion. The bulk magnetic susceptibility $\chi(T)$ of $Cu_{1.5}Co_{1.5}S_4$ has the Curie-Weiss-type paramagnetism with the AF peak at 19.0 K, as shown in Fig. 1(a). The present results of the linear dependence of the negative $K^{63}(T)$ on $\chi(T)$ and of the nearly T independent K^{59} in $Cu_{1.5}Co_{1.5}S_4$ indicate that the $3d$ hole band of Cu at the A site is mainly responsible for the spin paramagnetism. The $(T_1T)^{-1}$ of both ^{63}Cu and ^{59}Co is significantly enhanced at low T, but the divergence behavior of T_1^{-1} at $\sim T_N$ expected in the weak-itinerant AF substances was not observed. This is consistent with the results of specific heat measurement, which did not reveal any anomalies around T_N.[14] These results indicate that any long-range AF orders are not established below ~19 K.

Two characteristic results are obtained in the NMR experiment for the copper thiospinel $Cu_{1.5}Co_{1.5}S_4$: (i) very weak T dependence of K^{63} and nearly T-independent K^{59}; (ii) significant $(T_1T)^{-1}$ enhancements near T_c. These results agree qualitatively with those observed for the over hole-doped copper perovskite HTSC of $La_{2-x}Sr_xCuO_4$ (Ref. 9) and $YBa_2Cu_3O_7$ (Ref. 10). The unusual Cu relaxation behavior in HTSC, associated with the growth of AF spin correlations, is the subject of great interest and has been extensively studied. The essential point is that, as the $(T_1T)^{-1}$ is expressed in terms of the dynamical spin susceptibility,

$$(T_1T)^{-1}=\frac{\gamma^2k_B}{2\mu_B^2}\sum_q\frac{A_q^2\mathrm{Im}\chi_q(\omega)}{\omega}, \qquad (4)$$

a growth of the staggered susceptibility $\chi_Q(T)$ at the zone boundary is responsible for the large $(T_1T)^{-1}$ enhancement, where $Q=(\pi/2,\pi/2)$ for the square lattice of HTSC.

Thus we may consider that the AF spin correlations play an important role on the magnetism and the SC formation not only in HTSC but also in $Cu_{1.5}Co_{1.5}S_4$, although there seems no evident structural resemblance between the thiospinel and HTSC. It is worth to mention that a non-SC compound of $CuCo_2S_4$, on the other hand, did not reveal such a considerable amount of enhancement in $(T_1T)^{-1}$ in our preliminary ^{59}Co PQR study.

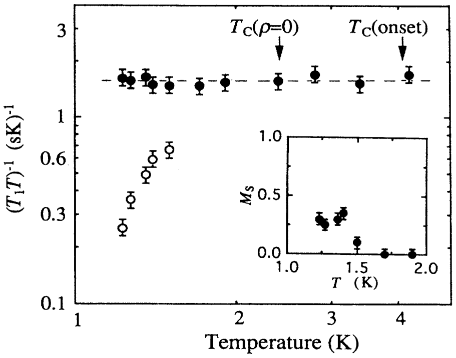

FIG. 5. Temperature dependence of $(T_1T)^{-1}$ of ^{59}Co in $Cu_{1.5}Co_{1.5}S_4$ obtained by PQR in the superconducting state: ●, $(T_{1(f)}T)^{-1}$; ○, $(T_{1(s)}T)^{-1}$. The inset shows the temperature dependence of the fractional component M_s with the slow relaxation rate $T_{1(s)}^{-1}$.

The T dependence of T_1 below T_c for the conventional BCS superconductors is well established:[15] the isotropic SC energy gap Δ is opened at the Fermi level below T_c. This causes a T_1^{-1} enhancement (BCS coherence peak) just below T_c and an exponential decrease at lower T. The magnitude of the BCS coherence peak is known to be diminished when anisotropy of the energy gap $\delta\Delta$ exists and/or the external magnetic field is applied. In the case of HTSC, on the other hand, the behavior of T_1 in the SC state has converged as follows: T_1^{-1} decreases rapidly just below T_c without the BCS coherence peak, but exhibits different behavior at lower T in each case.

In the present case of $Cu_{1.5}Co_{1.5}S_4$, the experimental T dependence of T_1 of ^{59}Co below T_c is not simply explained within the framework of the conventional BCS model, nor is it an analogy of the T_1^{-1} behavior in HTSC. T_1^{-1} of the dominant fraction of Co at the B sites follows roughly the $(T_1T)^{-1}\simeq1.5$ (sK)$^{-1}$ relation down to 1.23 K, in spite of the fact that T_1 was measured under zero external magnetic field. T_1^{-1} of the partial fraction of Co appeared below $\sim0.65T_c$, however, shows a rapid decrease, providing evidence for the partial formation of the SC energy gap. As the Meissner effect emerges below T_c(onset)~4.0 K and presents ~100% diamagnetism at 1.23 K, we may consider that the dominant part of the specimen is in a gapless SC state down to 1.23 K, possibly caused by the strong AF spin correlations. However it cannot be ruled out the possibility that a considerable part of the specimen is still in the normal state down to 1.23 K because there is a case in which ~100% diamagnetism does not correspond to the perfect Meissner effect. Further experimental study and analysis of the T_1 behavior in the SC state at lower temperatures and of the dependence of the $(T_1T)^{-1}$ enhancement on the Cu substitution content x are in progress.

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