Effect of Zn substitution for Cu on Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$

Kohki H. Satoh, Masatoshi Hiraiishi, Masanori Miyazaki, Soshi Takeshita, Akihiro Koda, Ryosuke Kadono, Ikuya Yamada, Kengo Oka, Masaki Azuma, Yuichi Shimakawa, and Mikio Takano

Department of Materials Structure Science, The Graduate University for Advanced Studies (Sokendai), Tsukuba, Ibaraki 305-0801, Japan

Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK), Tsukuba, Ibaraki 305-0801, Japan

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Abstract

A weakening of superconductivity upon substitution of Cu by Zn (0.5–1%) is observed in a high-$T_c$ cuprate, Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$, near the hole concentration of 1/8 per Cu. The superconducting transition temperature and its volume fraction, estimated by magnetic susceptibility, exhibit a sizable anomaly for $x = 0.12–0.14$, where the slowing down of Cu spin fluctuations below 5 K is demonstrated by muon spin relaxation experiments. These observations are in close resemblance to other typical cuprates including YBa$_2$Cu$_3$O$_{7-\delta}$, and Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$, providing further evidence that Zn-induced “stripe” correlation is a universal feature of high-$T_c$ cuprate superconductors common to that of La$_{2-x}$A$_x$CuO$_4$ (A=Ba, Sr).

Key words: high-$T_c$ cuprates, 1/8 anomaly, stripe correlation, µSR

1. Introduction

It is established that the superconducting transition temperature ($T_c$) is suppressed near the hole concentration $p \sim 1/8$ in La$_{2-x}$Ba$_x$CuO$_4$ (LBCO) and La$_{2-x-y}$Nd$_y$Sr$_2$CuO$_4$ (LNSCO), where a charge- and spin-stripe order develops in place of superconductivity [1,2]. A similar tendency has been reported for La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) with a slight shift of $x$ for the strongest strip correlation [3]. This so-called “1/8 anomaly” has drawn considerable attention in view of a potential link to the mechanism of high-$T_c$ superconductivity in cuprates [4]. It has been shown that substitution of Cu by small amounts of Zn stabilize this stripe correlations, as it leads to the “1/8 anomaly” in a variety of cuprates including LSCO [5], YBa$_2$Cu$_3$O$_{7-\delta}$ (YBCO) [6], and Bi$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_{8+\delta}$ (BSCCO) [7]. However, it is still controversial whether this anomaly is a common feature in cuprates or that unique to the La214 system.

Here, we report on the 1/8 anomaly in Ca$_{2-x}$Na$_x$CuO$_2$Cl$_2$ (Na-CCOC) studied by magnetic susceptibility and muon spin relaxation (µSR). While Na-CCOC has a similar structure to La$_{2-x}$Sr$_x$CuO$_4$, it is characterized by flat CuO$_2$ planes even at low temperatures owing to substitution of apical oxygen with chlorine in the CuO$_6$ octahedra. This is in marked contrast to the case of LSCO or LBCO...
that have a periodic distortion of the CuO$_2$ planes at low temperatures. The excellent cleavability of Na-CCOC crystals makes it feasible to investigate the electronic properties using surface-sensitive measurements such as angle resolved photoemission spectroscopy (ARPES) and scanning tunneling microscopy and spectroscopy (STM/STS). The latter reports the occurrence of a checkerboard-like electronic modulation and the coexistence of charge order and superconductivity [8], which exhibits a good correspondence with the inhomogeneous (spin glass-like) magnetic ground state revealed by $\mu$SR [9]. Meanwhile, the previous search for the 1/8 anomaly in Na-CCOC came to a negative result [10].

Considering that Zn substitution enhances stripe correlations in other cuprates, we prepared Zn-free and Zn substituted Na-CCOC samples near the hole concentration of 1/8 per Cu, and searched for the 1/8 anomaly in this compound by means of magnetization and muon spin relaxation ($\mu$SR) measurements.

2. Experimental details

Polycrystalline samples of Na-CCOC were prepared by high-pressure synthesis techniques. Ca$_2$CuO$_2$Cl$_2$ and Ca$_2$Cu$_{0.9925}$Zn$_{0.0075}$O$_2$Cl$_2$, prepared by solid state reaction of Ca$_2$CuO$_3$, CuO, ZnO, CaCl$_2$ in N$_2$ flow with several grindings under ambient pressure, were mixed with NaClO$_4$ and CuO, and then sealed in a cylindrical capsule made out of gold. High pressure synthesis was performed using a cubic anvil-type high pressure apparatus operated under 6 GPa at a maximum temperature of 1000°C. Due to the extreme high hygroscopicity of Na-CCOC, all manipulations of the samples were carried out in glove-boxes filled with Ar. All samples (with varying $x$) were confirmed to be of single phase by means of X-ray diffraction measurements. Their structure is $I4/mmm$ space group at room temperature, where the lattice parameters change continuously as $x$ varies. More specifically, the $a$-axis shrinks as the Na concentration increases, indicating that hole carriers are introduced into the CuO$_2$ plane while the $c$-axis expands. The magnetic susceptibility was measured using a superconducting quantum interference device (MPMS, Quantum Design Co.), where the measurements were made while the temperature was scanned upwards after field cooling of 20 Oe. Conventional $\mu$SR measurements were performed on the M15 beamline of TRIUMF (Vancouver, Canada).

3. Result and Discussion

Fig. 1(a) shows the Na doping dependence of $T_c$, where $T_c$ is defined as the temperature at which the temperature gradient of the magnetic susceptibility, $d\chi/dT$, is at its maxima. The error bars in Fig. 1(a) are evaluated from the spread of $\chi$ around $T_c$ and that of $T_c$ itself among several samples with the same $x$. For Zn-free samples, $T_c$ exhibits a monotonous increase with Na doping between $x=0.11$ and 0.15. In contrast, an overall reduction of $T_c$ is observed for Zn substituted samples ($y = 0.005$) as compared with Zn-free ones. Moreover, $T_c$ shows a clear trend of leveling off around 13 K for $0.12 \leq x \leq 0.135$, which is followed by a jump to $\sim 18$ K at $x=0.14$. This step-like behavior is similar to the one observed in Zn substituted YBa$_2$Cu$_3$O$_{7-\delta}$ [8]. Fig. 1(b) shows the Na doping dependence of the superconducting volume fraction estimated from the diamagnetic susceptibility at 5 K. The fraction in Zn-substituted samples is also reduced as compared with that in Zn-free samples. Furthermore, a step-like change is also observed near 1/8 hole concentration in line with the case of $T_c$. Thus, the 1/8 anomaly is clearly observed as anomalies of both $T_c$ and the superconducting volume fraction in Na-CCOC upon Zn-substitution for Cu.

We have performed $\mu$SR experiments to investigate the microscopic details of this anomaly. As has been demonstrated in earlier reports [8-10], $\mu$SR serves as a sensitive local magnetic probe that covers a unique time window of observation ($10^{-9} - 10^{-5}$ s) complementary to other magnetic probes like neutron diffraction and nuclear magnetic resonance. It does not rely on the long-range coherence of any magnetic order, and therefore is useful to examine the random local magnetism, e.g., a spin-glass state.

Fig. 2 shows $\mu$SR spectra measured under zero external field conditions (ZF) in Ca$_{2-x}$Na$_x$Cu$_{1-y}$Zn$_y$O$_2$Cl$_2$ for (a) Zn-free samples ($x = 0.14$, $y = 0.00$) and (b) 0.5% of Zn substitution for Cu ($x = 0.125$, $y = 0.005$). We observe a Gaussian depolarization due to random local fields from nuclear moments in the Zn-free samples over the entire temperature range down to 2 K. Meanwhile, in the latter case, an exponential damping is observed in the compound with Zn-substitution at 2 K. The spectra suggest a slowing down of Cu spin fluctuations with decreasing temperature below $\sim 5$ K. A similar phe-
The phenomenon associated with Zn substitution was also reported for the case of the La214 systems, YBCO, and BSCCO, and it suggests that the Zn impurity effect is a common feature of High-Tc cuprate superconductors. However, it must be noted that the Cu spins are not completely static nor in any long-range ordered state at 2 K, as inferred from the absence of a spontaneous oscillatory signal in the \( \mu \)SR time spectrum. This might be because the temperature is still too high to freeze out the Cu spins.

The \( \mu \)SR time spectra (=asymmetry) are analyzed by fits using the following form,

\[
AP(t) = [A_1 + A_2 \exp(-\lambda t)]G_{\text{DKT}}(\Delta, \nu, t),
\]

where the first term represents a signal from muons stopping in a non-magnetic region. The second term represents that of magnetic regions in which the muon senses Cu spin fluctuations, \( A_i \) are the partial asymmetries which are proportional to the respective volume fractions, \( \lambda \) is the depolarization rate, and \( G_{\text{DKT}}(\Delta, \nu, t) \) is the Kubo-Toyabe function that represents the Gaussian damping due to nuclear random local fields (with \( \Delta \) being the linewidth and \( \nu \) the fluctuation rate of the nuclear random local fields).

As shown in Fig 3 \( \lambda \) is almost zero in Zn-free samples \( [x=0.14, y=0.00 (T_c \sim 22 \text{ K}), x=0.0125, y=0.00 (T_c \sim 17 \text{ K})] \) and in the sample with \( x \neq 1/8 \ [x=0.15, y=0.01 (T_c \sim 10 \text{ K})] \), where the non-magnetic region dominates over the entire sample volume. On the other hand, it increases below 5 K in Zn-substituted samples near \( x \sim 1/8 \ [x=0.0125, y=0.005 (T_c \sim 13 \text{ K}) \) and \( x=0.0125, y=0.01 \) (not superconducting)]. Thus, it is inferred from ZF-\( \mu \)SR
experiments that the 1/8 anomaly observed in bulk properties is associated with the slowing down of Cu spin fluctuations in Na-CCOC.

In LBCO and LNSCO near \( x \approx 1/8 \), the appearance of an incommensurate spin density wave (SDW) phase and an associated suppression of superconductivity has been reported within the present range of temperature [11]. The absence of (or the reduction of the characteristic temperature for) such a static SDW phase in Na-CCOC may be attributed to that of the structural phase transition which is known to occur in La214 systems [12]. In LBCO at \( x=1/8 \), the lattice structure exhibits a successive change with decreasing temperature from a high-temperature tetragonal (HTT) phase at room temperature to a low-temperature orthorhombic (LTO) phase, and then to a low-temperature tetragonal (LTT) phase. Each phase is different in symmetry with respect to the distortion along the CuO\(_2\) planes, and the SDW phase occurs in accordance with the LTT phase in LBCO. Meanwhile, in the case of LSCO that does not exhibit the LTT phase, the suppression of superconductivity is relatively weak. Since Na-CCOC remains in the HTT phase over the entire temperature range of observation (> 2 K), the absence of the static SDW phase near \( x = 1/8 \) may suggest a common trend that the LTT phase stabilizes the SDW phase (by “pinning the dynamical stripe”). However, it is reported that Zn substitution for Cu enhances the SDW state in LSCO [5], and that the SDW phase survives in spite of the suppression of the LTT phase by applying hydrostatic pressure [13]. These observations might in turn point to the reversed role of cause and effect between the instability towards the SDW phase and the occurrence of LTT phase. The present result would make a strong case for the SDW instability as an intrinsic feature of the CuO\(_2\) planes irrespective of the LTT phase.

It might be speculated that the electronic state of the Cu ions are sensitive to the local lattice distortion (but not to the long range lattice morphology) so that the local impurities like Zn have relatively strong influence on the SDW instability. In this regard, another factor would be the degree of A-site disorder that is known to be different between LBCO and LSCO. Eisaki et al. reported that the A-site disorder has a certain influence on \( T_c \) [11], suggesting that the CuO\(_2\) planes are strongly affected by the A-site ions.

In conclusion, we demonstrated the presence of the 1/8 anomaly in \( Ca_{2−x}Na_xCu_{1−y}Zn_yO_2Cl_2 \) with a small fraction of Cu substituted by Zn. Such an anomaly is also observed in many families of cuprates near the hole doping concentration of 1/8, and it suggests that the SDW instability against local distortion of the CuO\(_2\) planes is a common feature of high-\( T_c \) cuprate superconductors.

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