1/8 anomaly in the excess-oxygen-doped La$_{1.8}$Nd$_{0.2}$Cu$_{1-y}$Zn$_y$O$_{4+\delta}$


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I. INTRODUCTION

The so-called 1/8 anomaly, namely, the anomalous suppression of superconductivity at $p$ (the hole concentration per Cu) = 1/8 in the high-$T_c$ superconductors has attracted great interest in relation to the stripe correlations of spins and holes and also to the mechanism of the high-$T_c$ superconductivity. The 1/8 anomaly was discovered for the first time in La$_{1.85}$Nd$_{0.2}$Cu$_{1-y}$Zn$_y$O$_4$+$\delta$, where the excess oxygen is doped by the electrochemical technique and the phase separation of the excess oxygen is suppressed. The 1/8 anomaly has become marked by the 1% substitution of Zn for Cu. The muon-spin-relaxation measurements have revealed that the magnetic correlation develops at low temperatures below about 50 K in both Zn-free and 1% Zn-substituted samples with $p = 1/8$. Clear precession of muon spins suggesting the formation of a long-range magnetic order has been observed below 1 K in the 1% Zn-substituted sample with $p = 1/8$. These results are consistent with the stripe-pinning model.

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room temperature.\textsuperscript{17,18} The phase separation was found to be suppressed by the partial substitution of the trivalent Bi or Nd for the trivalent La on account of the random potential introduced into the LaO plane.\textsuperscript{19–21} Accordingly, Kato \textit{et al.} investigated the detailed $p$ dependence of the superconducting transition temperature, $T_{\text{c}}$, in the excess-oxygen-doped La$_{2-x}$Bi$_x$CuO$_{4+\delta}$ (LBCO) ($0.05<x<0.10$), changing $\delta$ finely, where the excess oxygen was doped by annealing under high pressures of oxygen\textsuperscript{22,23} or by the KMnO$_4$ oxidation method.\textsuperscript{24} They succeeded in observing a continuous increase in $T_{\text{c}}$ with increasing $\delta$ in the underdoped regime, which was almost similar to that observed in LSCO. However, the 1/8 anomaly was not observed in LBCO, where the crystal structure remained in the tetragonal high-temperature (THT) phase (space group: I4/mmm) even at low temperatures for $p<1/8$.

In this paper, in order to search for the 1/8 anomaly in the excess-oxygen-doped La-214 system, we have prepared the excess-oxygen-doped La$_{1.8}$Nd$_{0.2}$Cu$_{1-y}$Zn$_y$O$_4+\delta$ (LNCZO), where the excess oxygen is doped by the electrochemical technique and the phase separation of the excess oxygen is suppressed by the 10% substitution of Nd for La. Here, Zn atoms are introduced so as to pin the possible dynamical stripes. We have investigated the thermoelectric power, electrical resistivity, and $T_{\text{c}}$ of the excess-oxygen-doped LNCZO with $y=0$ and 0.01, changing $\delta$ finely. Muon-spin-relaxation ($\mu$SR) measurements have been performed to study the Cu-spin state. Powder x-ray diffraction measurements have also been carried out in a wide temperature range between 10 K and room temperature to study the crystal structure.

II. EXPERIMENT

Sintered samples of the Zn-free ($y=0$) and 1% Zn-substituted ($y=0.01$) La$_{1.8}$Nd$_{0.2}$Cu$_{1-y}$Zn$_y$O$_4$ were prepared by the solid-state reaction method from appropriated powders of La$_2$O$_3$, Nd$_2$O$_3$, CuO, and ZnO. The powders were mixed and prefired in air at 900 °C for 12 h. After pulverization, the prefired materials were mixed, pelletedized, and sintered in air at 1050 °C for 24 h, followed by furnace cooling. This sintering process was carried out once again to obtain homogeneous samples. Before the incorporation of excess oxygen, the sintered samples were annealed in flowing Ar gas at 700 °C for 48 h to remove excess oxygen incorporated during the sintering process. These samples were characterized by powder x-ray diffraction at room temperature to be of the single phase and confirmed by iodometric titration to contain no excess oxygen within the experimental accuracy.

The excess-oxygen doping was made by the electrochemical oxidation method\textsuperscript{25} using a potentiostat-galvanostat (Hokuto Denko Co., Model HABF-501). A three-electrode cell was set up as La$_{1.8}$Nd$_{0.2}$Cu$_{1-y}$Zn$_y$O$_4$ aqueous solution of KOH/Pt, where the working electrode was a pellet of La$_{1.8}$Nd$_{0.2}$Cu$_{1-y}$Zn$_y$O$_4$ with the dimensions of ~10 mm in diameter and ~1 mm in thickness and the counter electrode was a Pt wire. As an electrolyte, an aqueous solution of KOH (1.0 mol/l) was used at 60 °C. A Hg/Hg$_2$Cl$_2$ electrode was used as a reference electrode connected to the aqueous solution of KOH via the salt bridge. The excess-oxygen doping was carried out at a constant voltage of ~300 mV. After the excess-oxygen doping, the pellet was washed with anhydrous ethanol and dried in air at 100 °C for 24 h. The amount of the excess oxygen doped into the pellet was estimated by Faraday’s law of electrolysis. That is, it was calculated from the amount of the electrical charge that flowed in the pellet, based upon the following chemical reaction:

$$\text{La}_{1.8}\text{Nd}_{0.2}\text{Cu}_{1-y}\text{Zn}_y\text{O}_4 + 2\delta\text{OH}^- \rightarrow \text{La}_{1.8}\text{Nd}_{0.2}\text{Cu}_{1-y}\text{Zn}_y\text{O}_4+\delta + \delta\text{H}_2\text{O} + 2\delta\text{e}^-.$$ (1)

Values of the excess oxygen estimated thus were confirmed to be almost the same within the experimental accuracy as those estimated by iodometric titration.

Powder x-ray diffraction measurements were made using a conventional diffractometer with a curved graphite monochromator for CuK$_\alpha$ radiation. The data were analyzed after CuK$_{\alpha2}$ stripping. Thermoelectric power measurements were carried out by the dc method with a temperature gradient of ~0.5 K across the sample. Electrical resistivity measurements were carried out by the dc four-probe method. $\mu$SR measurements were performed in zero field at low temperatures down to 0.3 K at the RIKEN-RAL Muon Facility at the Rutherford-Appleton Laboratory in the UK. A pulsed positive surface-muon beam with a momentum of 27 MeV/c was used. The asymmetry parameter $A(t)$ was defined as $A(t) = (F(t) - \alpha B(t)) / (F(t) + \alpha B(t))$, where $F(t)$ and $B(t)$ are total muon events counted by the forward and backward counters at time $t$, respectively.

III. RESULTS

A. Crystal structure

Figure 2 shows the variation of the lattice parameters with $\delta$ at room temperature obtained from the powder x-ray diffraction measurements. The crystal structure is orthorhombic for all samples with $0<\delta<0.10$. The lattice parameter $c$ increases monotonically with increasing $\delta$, suggesting that the excess oxygen is continuously inserted between the LaO-LaO planes. As for the homogeneity of the excess oxygen, it is naively guessed that the excess-oxygen content is larger in the surface area of the pellet in contact with the aqueous solution of KOH than in the internal part. However, the $c$ value does not change between the surface area and the internal part, so that the excess oxygen is concluded to be homogeneously doped into the pellet within the accuracy of the powder x-ray diffraction measurements. It is found that the orthorhombicity decreases with increasing $\delta$ for $\delta<0.05$, while it increases for $\delta>0.05$. The space group of the orthorhombic phase for $\delta<0.05$ is guessed to be Bnnb, as in the case of the lightly excess-oxygen-doped regime of LCO (Refs. 17 and 18) and LBCO.\textsuperscript{22,24} For $\delta>0.05$, on the other hand, the orthorhombic phase with the space group Fmmm may appear, as in the case of the heavily excess-oxygen-doped regime of LCO (Refs. 17 and 18) and LBCO.\textsuperscript{21,22,24}
Upper panels of Fig. 3 display the powder x-ray diffraction profiles of the (110)\textsubscript{THT} reflection at various temperatures for the typical samples with \(d = 0.049, 0.0625,\) and 0.086. The suffix THT indicates an index in the THT phase. All the (110)\textsubscript{THT} peaks are found to clearly split into two, meaning that the crystal structure is orthorhombic. The orthorhombicity is found to increase with decreasing temperature for these samples. This is clearly seen in the lower panels of Fig. 3, where the temperature dependence of the full width at half maximum (FWHM) of the (110)\textsubscript{THT}, (213)\textsubscript{THT}, and (220)\textsubscript{THT} peaks is shown. The increase of the orthorhombicity with decreasing temperature is most marked in \(d = 0.049\) among these samples and is comparable to that generally observed in the OMT phase of the La-214 system. This is consistent with the above guess that the space group for \(d < 0.05\) is Bmab. Moreover, what is significant is that neither symptom of the phase transition to the TLT phase nor the phase separation of the excess oxygen are observed at low temperatures down to 10 K for these samples.

B. Thermoelectric power and electrical resistivity

Figure 4 displays the temperature dependence of the thermoelectric power \(S\) for various \(d\) values. The value of \(S\) decreases with increasing \(d\). Taking \(p = 2d\), this is a typical behavior observed in the hole-doped high-\(T_c\) cuprates.\textsuperscript{26} In fact, the \(d\) dependence of the value of \(S\) at 290 K, \(S\textsubscript{290K}\), is similar to that of LSCO,\textsuperscript{27} as shown in Fig. 5. This suggests that the CuO\(_2\) plane is continuously supplied with holes with increasing \(d\).

Figure 6 displays the temperature dependence of the electrical resistivity \(\rho\) for various \(d\) values. The value of \(\rho\) de-
creases with increasing $\delta$, namely, with increasing $p$. A metallic behavior ($d\rho/dT > 0$) is observed in the high-temperature region, while an upturn behavior of $\rho$ ($d\rho/dT < 0$) is observed at low temperatures below about 100 K for $\delta \leq 0.07$. The superconducting transition appears for $\delta > 0.025$. The $\rho$ dependence of $T_c$, defined as the midpoint of the superconducting transition curve in the $\rho$ vs $T$ plot, is shown in the lower panel of Fig. 7. The $\delta$ dependences of $\rho$ and $T_c$ are different from those of LCO where the phase separation of the excess oxygen occurs. Taking $p = 2\delta$, the $\rho$ dependences of $\rho$ and $T_c$ are similar to those of LSCO, respectively. These results also suggest that the phase separation of the excess oxygen is suppressed and that the doped excess-oxygen supplies the CuO$_2$ plane with holes homogeneously. What is remarkable is that a small dip of $T_c$ is observed in the $\delta$ dependence of $T_c$ around $\delta = 0.0625$ ($p = 1/8$), which is very similar to that observed in LSCO around $p = 1/8$. It is noted that the superconductivity at $\delta = 0.0625$ is confirmed to be of the bulk from the magnetic susceptibility measurement. The upturn behavior of $\rho$ is generally observed at low temperatures in the underdoped regime of the high-$T_c$ cuprates, which is understood to be due to localization of carriers. The degree of the localization may be estimated by the value of $(\rho_{\text{max}} - \rho_{\text{min}})/\rho_{\text{min}}$, where $\rho_{\text{min}}$ and $\rho_{\text{max}}$ are defined as the minimum value of $\rho$ around 100 K and the maximum value of $\rho$ just above $T_c$, respectively. As shown in the upper panel of Fig. 7, $(\rho_{\text{max}} - \rho_{\text{min}})/\rho_{\text{min}}$ roughly decreases with increasing $\delta$, namely, with increasing $p$. However, a small hump is observed around $\delta = 0.0625$, which is similar to that observed around $p = 1/8$ in LBCO. Therefore, the small dip of $T_c$ around $\delta = 0.0625$ is regarded as the very 1/8 anomaly.

The same measurements were carried out in the 1% Zn-substituted samples also. As shown in the upper panel of Fig. 7, $(\rho_{\text{max}} - \rho_{\text{min}})/\rho_{\text{min}}$ increases as a result of the 1% Zn-substitution for each $\delta$. It exhibits a hump around $\delta = 0.0625$ in the Zn-substituted samples as well as in the Zn-free ones. On the other hand, $T_c$ decreases as a result of the 1% Zn-substitution for each $\delta$. The dip of $T_c$ around $\delta = 0.0625$ becomes marked in the Zn-substituted samples, as in the case of LSCO. It is noted from the magnetic susceptibility measurement that the superconductivity in the Zn-substituted sample with $\delta = 0.0625$ is not of the bulk, compared with the bulk superconductivity in the Zn-free sample with $\delta = 0.0625$. Accordingly, it appears that the 1% Zn-substitution enhances the 1/8 anomaly.
C. Muon spin relaxation

Figure 8 displays the $\mu$SR time spectra, namely, the time evolution of $A(t)$ in zero field for the Zn-free ($y=0$) and 1% Zn-substituted ($y=0.01$) La_{1.8}Nd_{0.2}Cu_{1-y}Zn_{y}O_{4+\delta} with $\delta=0.0625$ ($p=1/8$). In both Zn-free and Zn-substituted samples, the time spectrum shows a Gaussian-type depolarization behavior at high temperatures above 60 K, indicating that the Cu spins are fluctuating so fast as not to affect the muon spins. In the both samples, the depolarization behavior deviates from the Gaussian-type at low temperatures below 60 K and a fast depolarizing component appears, meaning that the Cu-spin fluctuations exhibit a slowing-down behavior on account of the development of the magnetic correlation at low temperatures. Even at the lowest temperature of 0.3 K, the dynamical long-time relaxation behavior is observed, which may be due to the Nd moments. In the Zn-substituted sample, muon-spin precession is observed at very low temperatures below 1 K, as clearly seen in Fig. 9, indicating the appearance of a long-range ordered state of Cu spins.

The two-component function $A(t)=A_0 e^{-\lambda t}G_0(\Delta,t)+A_1 e^{-\lambda t}f(t)$ is used conventionally in order to analyze the

![Figure 9](image9.png)
IV. DISCUSSION

We have found the 1/8 anomaly and also a magnetic transition at $\delta = 0.0625$ ($p = 1/8$) in both Zn-free and 1% Zn-substituted LNCZO. Moreover, the internal field at low temperatures in the 1% Zn-substituted LNCZO with $\delta = 0.0625$ is almost the same as that in the 1% Zn-substituted LSCO with $p = 1/8$, suggesting that the spin structures are similar to each other. Accordingly, it is very likely that the static stripe order is formed at $\delta = 0.0625$ in both Zn-free and 1% Zn-substituted LNCZO as well as in LSCO. The 1/8 anomaly has been found to become marked by the 1% substitution of Zn for Cu in LNCZO, as in the case of LSCO. Furthermore, the muon-spin precession is clearly observed in the Zn-substituted sample rather than in the Zn-free one, indicating that the magnetic order in the Zn-substituted sample is more long-ranged than that in the Zn-free one. These results are consistent with the stripe-pinning model, where the dynamical stripes are regarded as existing in the CuO$_2$ plane and tending to be statically stabilized at $p = 1/8$ and being effectively pinned by a small amount of Zn, leading to the appearance of the static stripe order and the suppression of superconductivity. As for the difference in $T_N$ between the Zn-free and 1% Zn-substituted samples, the effect of the spin dilution due to the substitution of the nonmagnetic Zn for the magnetic Cu may emerge at relatively high temperatures above ~10 K in the Zn-substituted sample, leading to the decrease in $T_N$. A similar effect by the Zn substitution has also been observed around $p = 1/8$ in the Zn-substituted LSCO. Once the Cu-spin fluctuations slow down at relatively low temperatures below ~10 K, on the other hand, Zn may operate to pin the dynamical stripes strongly, leading to the formation of a more long-ranged order in the Zn-substituted sample than in the Zn-free one.

Although the 1/8 anomaly has been found in the Zn-free LNCZO, no 1/8 anomaly has been observed in the excess-oxygen-doped LBCO, as mentioned in Sec. I. According to the stripe-pinning model, the reason may be as follows. The buckling of the CuO$_2$ plane in the TLT structure is known to be effective for the pinning of the dynamical stripes, because the rotation axis of the buckling is parallel to the stripes. On the other hand, the flatness of the CuO$_2$ plane is considered to be ineffective for the pinning. LBCO around $p = 1/8$ has the THT structure where the CuO$_2$ plane is flat. Therefore, the dynamical stripes are hard to be statically stabilized, leading to no 1/8 anomaly in LBCO. Actually, in thin films of LBCO where the CuO$_2$ plane is so deformed due to the lattice mismatch between the film and...
mation develops at low temperatures below about 50 K in both Zn-free and 1% Zn-substituted samples with $p = 1/8$. The magnetic transition temperature is estimated as 25 K and 17 K for the Zn-free and Zn-substituted samples, respectively. Clear precession of muon spins has been observed below 1 K in the 1% Zn-substituted sample with $p = 1/8$ rather than in the Zn-free sample, indicating that the magnetic order in the Zn-substituted sample is more long-ranged than that in the Zn-free sample. These results are consistent with the stripe-pinning model where the dynamical stripes are regarded as existing in the CuO$_2$ plane and tending to be statically stabilized at $p \sim 1/8$ and effectively pinned by a small amount of nonmagnetic impurities such as Zn, leading to the appearance of the static stripe order and the suppression of superconductivity at $p \sim 1/8$. Compared with the result in the excess-oxygen-doped LBiCO, it appears that the buckling of the CuO$_2$ plane is indispensable to the appearance of the 1/8 anomaly.

V. SUMMARY

We have found the 1/8 anomaly in the excess-oxygen-doped LNCZO, where the excess oxygen is doped by the electrochemical technique and the phase separation of the excess oxygen is suppressed. The 1/8 anomaly has become marked by the 1% substitution of Zn for Cu. It has been found from the $\mu$SR measurements that the magnetic corre-