Stripe order and superconductivity in the mechanically milled La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$

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Abstract. We examine the effect of mechanical milling on the superconducting transition temperature $T_c$ in stripe-ordered La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$ with $x$~1/8. The X-ray diffraction patterns of samples milled for 24h show that the orthorhombicity is slightly reduced, in addition to the reduction of crystallite size and the increase of lattice strain, by mechanical milling. The $T_c$ is enhanced by the mechanical milling, although the magnitude of the diamagnetic signal is largely suppressed. The enhancement of $T_c$ suggests that the static stripe is suppressed in the mechanically milled sample.

1. Introduction

In La-based cuprate superconductors, static charge and spin stripe, which markedly suppresses the superconductivity, has so far been studied intensively [1]. The typical materials with stripe order in cuprates are La$_{2-x}$Ba$_x$CuO$_4$ (LBCO) and La$_{2-x,y}$Nd$_y$Sr$_x$CuO$_4$ (LNSCO) with $x$~1/8. Both LBCO and LNSCO undergo structural phase transitions caused by tilting of CuO$_6$ octahedra [2-4]. In the structural transition from the high-temperature tetragonal structure (HTT) to the low temperature orthorhombic structure (LTO) at $T_o$, the CuO$_6$ octahedra tilt about (110) axis of HTT. In addition, in the structural transition from LTO to the low temperature tetragonal structure (LTT) at a lower temperature $T_1$, the CuO$_6$ octahedra tilt about (1-10) axis. In LTT phase, the oxygen sites (or Cu-O bonds) within Cu-O plane become inequivalent and are divided into two kinds, which is considered to be important for the charge stripe order.

The HTT-LTO and LTO-LTT structural phase transitions are suppressed by applying a pressure, leading to an increase of the superconducting transition temperature $T_c$ under pressure [5, 6]. It is noted that the increase of $T_c$ is obviously smaller just at $x$=1/8 than at doping levels higher and lower than $x$=1/8, even if the structural transition from LTO to LTT is completely suppressed under pressure [5, 7]. Recently the crystal structure and $T_c$ in HTT phase under pressure were examined in LNSCO and LBCO by X-ray diffraction [8, 9]. It was reported that the local tilt distortions of the CuO$_6$ octahedra in HTT phase under pressure is closely related to the incomplete recovery of $T_c$ just at $x$=1/8, although the detailed structure of charge and spin stripe in the local tilt distortions is still unclear. To totally understand the suppression of superconductivity by the stripe order, it will be important to investigate the relation among the stripe order, superconductivity, and local distortions.
In the present study, we performed the mechanical milling for $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ with $x \approx 1/8$ to introduce (local) distortions and/or lattice strain in the crystal structure, and investigated the effects of the mechanical milling on the superconductivity and the crystal structure.

2. Experiment

Powder samples $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ with $x=0.13$ were synthesized using standard solid-state chemical techniques. The starting materials $\text{La}_2\text{O}_3$, $\text{Nd}_2\text{O}_3$, $\text{CuO}$, and $\text{SrCO}_3$ were mixed in the appropriate ratios and sintered in flowing oxygen at a temperature $1080 \, ^\circ\text{C}$ for 24 hours. The crystal structure of LNSCO samples was examined by X-ray powder diffraction with Cu $K\alpha$ radiation. The superconducting transition temperature $T_c$ was determined from superconducting diamagnetic curve by using a superconducting quantum interface device (SQUID) magnetometer under 50e.

Mechanical milling were performed in a hardened steel vial with a steel ball in air, which markedly reduces contamination of container and ball materials to the sample even in a long milling time. The milling period was 24h in the present study.

3. Results and Discussion

Figure 1 shows the results of X-ray powder diffraction (XRD) for LNSCO ($x=0.13$, $y=0.4$) at room temperature with and without milling. The XRD pattern for 0h of milling can be fit well, assuming the low temperature orthorhombic (LTO) structure with $Cmca$ space group symmetry (figure 1(a)). The obtained lattice parameters are $a=5.3279 \, \text{Å}$, $b=13.1463 \, \text{Å}$, $c=5.3580 \, \text{Å}$, which are consistent with those already reported [3, 8]. We also carried out XRD experiments for the sample milled for 24h (figure 1(b)). The XRD pattern for 24h of milling can also be fit on the assumption of LTO structure, although the peak slightly changes in position and becomes broader. The obtained lattice parameters for the milled sample are $a=5.3166 \, \text{Å}$, $b=13.1607 \, \text{Å}$, $c=5.3448 \, \text{Å}$. It should be noted that the orthorhombicity, defined as $2(c-a)/(c+a)$, slightly decreases and the ratio $R=2b(a+c)$ increases by milling for 24h, suggesting that the tilt angle of the CuO$_6$ octahedra slightly decreases by mechanical milling [8, 9].

![Figure 1](image_url)

**Figure 1.** X-ray diffraction patterns of $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ ($x=0.13$) at room temperature (a) without and (b) with milling.
All the Bragg peaks are broadened by milling for 24h (figure 1). As shown in figure 2, the full width at half maximum (FWHM, $\beta$) of the peaks for 24h of milling is ~2 times broader in low $2\theta$ region and ~3 times broader in higher $2\theta$ region than that for 0h of milling. Such an increase of FWHM is mainly caused by two effects of milling on the crystal structure; one is the decrease of the crystallite size $D$ and the other the increase of the lattice strain $\varepsilon$. Here we evaluated quantitatively $D$ and $\varepsilon$ by fitting on the basis of the Williamson-Hall equation:

$$\beta^2 = \frac{X^2}{\cos^2\theta} + Y^2\tan^2\theta$$

where $X = 0.9\lambda/D$ and $Y = 4\varepsilon$. As shown in figure 2, the $\theta$ dependence of FWHM($\beta$) can be fit well using the Williamson-Hall equation. The obtained values of the fitting parameters are $D=110\text{ nm}$ and $\varepsilon=0.07\%$ for 0h of milling and $D=75\text{ nm}$ and $\varepsilon=0.24\%$ for 24h of milling. The $\varepsilon$-value for 24h of milling is consistent with the increase of the ratio $R=2b/(a+c)$, $\Delta R\sim0.3\%$, by milling. Thus one can confirm that the mechanical milling introduces the lattice strain in the crystal and reduces the crystallite size.

**Figure 2.** The full width at half maximum $\beta$ of various Bragg peaks for $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ ($x=0.13$) shown as a function of $2\theta$. Solid lines represent fitting curves.

**Figure 3.** Temperature dependence of the diamagnetic moment for $\text{La}_{1.6-x}\text{Nd}_{0.4}\text{Sr}_x\text{CuO}_4$ ($x=0.13$) with and without milling. Here the magnitudes of the diamagnetic moments for 0h and 24h of milling are scaled with each other.
In figure 3, we show superconducting diamagnetic moment $M$ of LNSCO samples milled for 0h and 24h. Here $T_c$ was determined by extrapolating the steepest part of $M$–$T$ curve to zero level. The $T_c$’s for the samples milled for 0h and 24h are ~8K and ~13K, meaning that $T_c$ is recovered to some extent by mechanical milling. Actually the magnitude of diamagnetic moment becomes smaller by ~15% in the milled samples. It is known that the particle size of powder samples is markedly reduced by mechanical milling, as well as the crystallite size. Then the reduction of the diamagnetic signal observed in the milled sample can be ascribed to the reduction of particle size. In figure 3, small upturns appear at low temperature below ~5K, leaving a minimum in the $M$–$T$ curve around a low temperature. The small upturns for both samples are mainly attributable to magnetic moments of Nd ions.

In the sample milled for 24h, the increase of $T_c$, $\Delta T_c$, is ~5K. The increase of $T_c$ suggests that the stripe order is suppressed to some extent by mechanical milling. The suppression of the stripe order and LTT structure has been reported in high pressure experiments [5-9]. In comparison with the high pressure experiment reported in LNSCO ($x$=0.12) by Crawford, the $\Delta T_c$ for 24h of milling is comparable to that under pressure of ~2GPa [8]. The orthorhombicity, corresponding to the tilt angle of the CuO$_6$ octahedra, is reduced to half value by applying a pressure of ~2GPa [8]. In the sample milled for 24h, the orthorhombicity decreases only by ~6%. This fact implies that the suppression of the tilt angle itself by mechanical milling will be too small to lead to sufficient suppression of LTT for $\Delta T_c$~5K. As mentioned above, in the sample milled for 24h, the lattice strain $\varepsilon$ increases largely and the $\varepsilon$-value is comparable to $\Delta R$. This may suggest that the lattice strain leads to inhomogeneous tilts of the CuO$_6$ octahedra in LTO, because $R$ is related to the tilting of the CuO$_6$ octahedra. Then we can speculate that the lattice strain introduced by mechanical milling may bring about a suppression of LTO-LTT transition at $T_1$ and the incomplete recovery of $T_c$. However we have no direct information about the crystal structure at low temperature in milled samples, and then the XRD experiments at low temperature is required to examine the effects of mechanical milling on LTT structure directly. In order to elucidate the increase of $T_c$ by mechanical milling, the detailed information about the relation among $\Delta T_c$, $D$ and $\varepsilon$ at low temperature will be required for various milling periods.

In conclusion, we carried out mechanical milling in stripe-ordered La$_{1.6-x}$Nd$_{0.4}$Sr$_x$CuO$_4$ with $x$=0.13. The $T_c$ increases from 8K to 13K by mechanical milling for 24h, suggesting the suppression of the stripe order by mechanical milling.

4. References

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