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Annealing effect on the electron-doped superconductor $Pr_{0.88}LaCe_{0.12}CuO_{4\pm\delta}$

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Using high-vacuum annealing treatment, the superconducting transition temperature T_c of the electron-doped $Pr_{0.88}LaCe_{0.12}CuO_{4\pm\delta}$ single crystals was successfully driven to a regime in which the T_c value continuously decreases with oxygen removal. This regime of oxygen-reduction process is hard to be understood according to the previous knowledge of this material. In addition, a remarkable relaxation of T_c over time was observed at room temperature, indicating that the variation in T_c is closely related to the rearrangement of oxygen in the sample. In combination with previous studies, it can be concluded that, in the whole process of oxygen reduction applied on $Pr_{0.88}LaCe_{0.12}CuO_{4\pm\delta}$, although the strength of antiferromagnetic (fluctuation) correlations does play a role, T_c is dominated by the disorder effect of CuO_2 plane either on copper sites or oxygen sites, which leads to a strong depairing effect.

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I. INTRODUCTION

It is well known that high T_c superconductivity can be induced in some copper oxides by doping holes into the parent compound which is proved to be an antiferromagnetic (AF) Mott insulator. While for electron-doped copper oxides such as $RE_{2-x}Ce_xCuO_{4\pm\delta}$ (RE=Pr,Nd,Sm,La) (RCCO), there is a long-standing issue that, besides doping carriers, annealing in a low-oxygen environment is necessary to induce superconductivity,[1,2] though the amount of the oxygen removed is extremely small, $\delta \sim 0.01-0.04$ (no more than 1%).[2] This oxygen-reduction annealing treatment drives the material continuously from an AF Mott insulator to a superconductor with very low normal-state resistivity,[3–8] accompanied by a sign change in Hall coefficient.[4,6,8] It was also suggested that oxygen-reduction process induces superconductivity by suppressing long-range AF order which seems to compete with superconducting order.[9–15] On all accounts, it is obvious that oxygen plays a significant role in the properties of these electron-doped superconductors, which has attracted plenty of interests.

In the T′ structured[1] RCCO, as shown in Fig. 1, there are two primary sites occupied by oxygen: O(1) in the CuO_2 plane and O(2) in the REO layer (RE=Pr,Nd,Sm,La). Apical oxygen should not exist in the ideal T′-structure materials, but in fact, neutron diffraction,[16,17] Mössbauer spectra,[18] Extended x-ray absorption fine structure measurements[19] and infrared crystal-field spectroscopy[20,21] suggested that there were tiny amount of oxygen occupying the apical site O(3). Although the role of doping oxygen is believed to induce holes into hole-doped cuprates such as $YBa_2Cu_3O_{7-\delta}$ (YBCO),[22,23] previous works on RCCO indicated that the reduction process could not be simply regarded as only increasing carrier density, alternatively, it reduces the disorder and impurity scattering by O(3) removal,[3,4,6,7,16,17] or destroys the long-range antiferromagnetic correlations by O(1) removal.[8,12,20,21] Moreover, a microscopic annealing process proposed by Kang *et al.* suggested that oxygen reduction repairs Cu deficiencies in the CuO_2 planes.[24] Up to now, the mechanism of the oxygen-reduction process is still an open question.

In this paper, we systemically studied the oxygen-reduction process in $Pr_{0.88}LaCe_{0.12}CuO_{4\pm\delta}$ (PLCCO) single crystals by using high-vacuum annealing. It was found that T_c gradually increased with oxygen removal and reached a maximum value of 25.9 K then decreased with further annealing. This T_c decreasing has not been realized previously in both PLCCO and $Pr_{2-x}Ce_xCuO_{4\pm\delta}$ (PCCO) and cannot be understood with the existing models. Another remarkable finding here is a relaxation of bulk T_c over time at room temperature. Combining these findings with previous studies, we suggest that T_c evolution in the whole oxygen-reduction process is dominated by the concentration of either Cu-site disorder or O-site disorder in CuO_2 plane, which has a close relationship with the pairing strength of Cooper pairs in electron-doped superconductors. These results should be helpful for understanding the mechanism of high-temperature superconductors (HTSC).

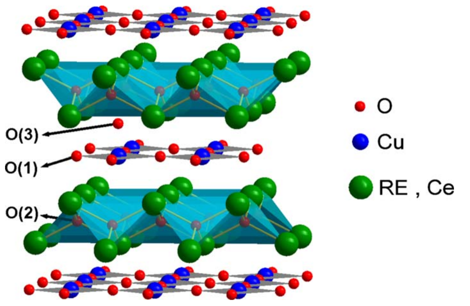

FIG. 1. (Color online) Crystal structure of $RE_{2-x}Ce_xCuO_{4\pm\delta}$. Three oxygen are denoted: O(1) in the CuO_2 plane, O(2) in the REO layer (RE=Pr,La in this paper), and a tiny amount of O(3) in the apical site.

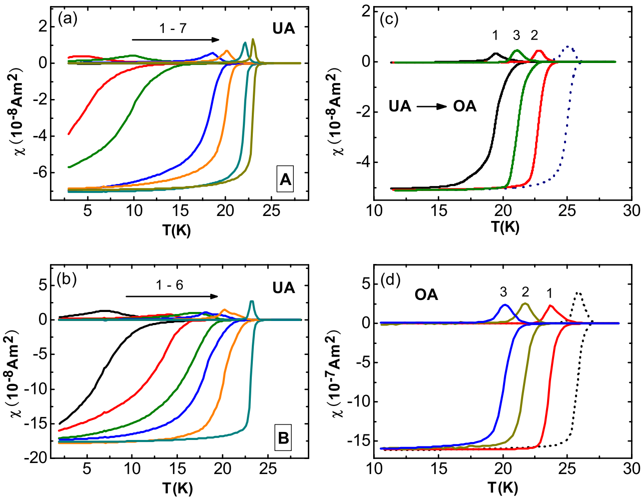

FIG. 2. (Color online) T_c evolution (indicated by ac susceptibility) with oxygen reduction in annealing processes, the increasing indexes indicate a decreasing of oxygen content. [(a) and (b)] UA regime: T_c increases with oxygen removal at different annealing temperatures (Table I). (c) A continuous oxygen-reduction process from UA or T_c-increasing regime to OA or T_c-decreasing regime. (d) OA regime: T_c decreases with oxygen removal. The dashed lines in (c) and (d) denote the highest T_c got on the corresponding samples.

II. EXPERIMENT

High quality single crystals of PLCCO were grown by the traveling-solvent floating-zone technique.[10] A dynamic annealing process was adopted to remove oxygen.[15] Small pieces (less than 40 mg) was used for avoiding inhomogeneity. High vacuum of $P < 3 \times 10^{-3}$ Pa was used to decrease the partial pressure of oxygen, which allows removing oxygen at a relatively lower temperature. The real annealing temperature T_r was hard to be exactly confirmed here due to a finite distance between the sample and the thermometer. Nonetheless, it can be estimated that T_r is about two hundreds of degrees higher than the setting temperature T_s. T_s was chosen to be in the range of 500 °C $< T_s <$ 620 °C by considering an appropriate annealing duration. In general, higher T_s leads to faster annealing. The oxygenated process was done in atmosphere at 400 °C (real value).

Critical temperature T_c was defined by the peak position of the imaginary part of the asusceptibility measured at zero field (zero-field cooled), it was measured in an *Oxford* cryogenic system (Maglab-EXA-12) or a superconducting quantum interference device (Quantum Design). The resistivity and Hall-coefficient measurements were done in a physical properties measurement system (Quantum Design), where the magnetic field was applied parallel to the *c* axis of the crystal. All the samples studied here were cut from one single crystal.

III. RESULTS AND DISCUSSIONS

A. Phase diagram of T_c evolution

TABLE I. Annealing parameters for the processes A and B. The sign of "+" means the additional time following the former Step.

Process	Index	Vacuum (10^{-3} Pa)	T_s (°C)	Time (h)	T_c (K)
A	(1)	<3	560	10	
	(2)	<3	560	+6	5.0
	(3)	<3	560	+4	10.0
	(4)	<3	560	+4	18.5
	(5)	<3	560	+4	20.1
	(6)	<3	560	+4	22.1
	(7)	<3	560	+4	23.0
B	(1)	<3	610	5	7.0
	(2)	<3	520	+3	14.0
	(3)	<3	500	+5	17.2
	(4)	<3	600	+1	18.2
	(5)	<3	600	+1.7	20.2
	(6)	<3	550	+6	23.2

Figures 2(a) and 2(b) show the T_c evolution in the dynamic annealing processes numbered as A and B. The corresponding annealing parameters are presented in Table I. In both cases of A and B [Figs. 2(a) and 2(b), respectively], T_c increases continuously in the annealing process, indicating that oxygen can be removed at all temperatures adopted here. Moreover, the content of removed oxygen depends on both the annealing temperature and the annealing time. An interesting find here is that if the annealing process continues in an appropriate temperature, T_c will turn around to decrease. Figure 2(c) shows such a continuous oxygen-reduction process in which T_c increases at first similar to the processes of A and B, and then decreases significantly though the optimal annealing with maximum T_c was overshot due to the annealing parameters is variable from one process to another, the dashed curve denotes the highest T_c we got on this sample. Since the T_c decreasing with oxygen reduction always follows the optimal annealing, it is thus ascribed to an overannealing (OA) regime in this work. Correspondingly, the T_c-increasing regime mentioned above is called underannealing (UA) regime. Figure 2(d) shows the OA regime realized on one sample, the dashed curve indicates the maximum T_c we got on this sample.

The UA regime is consistent with the previous reports.[7,8,25,26] However, the OA regime revealed in this work has never been achieved previously in the same material. Actually, this regime was only noticed in some early works focusing on $Nd_{2-x}Ce_xCuO_{4\pm\delta}$ (NCCO) thin films.[4,5] Among the previous studies on the UA regime many experiments indicated that T_c gradually increases to a saturated value with the oxygen removal,[7,8,25,26] and some recent works on PCCO thin films[8] and NCCO polycrystals[26] even suggested that the samples would be decomposed with further deoxygenated annealing. However, in this work, we demonstrate in the single crystals that this OA regime is really a bulk characteristic of electron-doped cuprates in which the sample is not decomposed while T_c decreases with the oxygen removal. The advances achieved here maybe benefit from

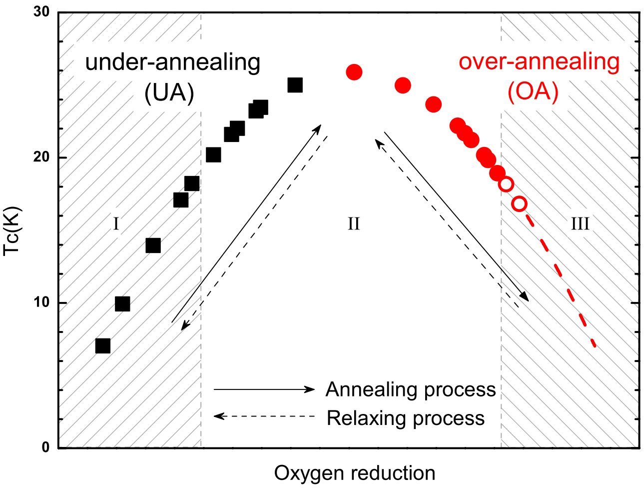

FIG. 3. (Color online) T_c versus oxygen reduction. The solid arrow lines indicate the direction of annealing process and the dot arrows indicate the direction of relaxing process. The horizontal axis data is in an arbitrary unit since the real oxygen content is hard to be obtained.

the low annealing temperatures, short annealing time, and the higher stability of a single crystal compared to that of a thin film or a polycrystal sample. The dynamic annealing process in high vacuum extends the temperature range of oxygen reduction,[27] which allows removing oxygen at a relatively low temperature and protects the sample from decomposition. In contrast to the previous experiments on thin films,[4,5] the susceptibility measurements on our single-crystal samples can undoubtedly demonstrate that the superconducting volume does not change with annealing process from UA regime to OA regime [refer to Figs. 2(a)–2(d)] and thus indicate that the decrease in T_c in OA regime is a bulk effect without decomposition.

In Fig. 3, we sum up the phase diagram of T_c with respect to the oxygen content. Since the real oxygen content is hard to be confirmed, we assume a domelike T_c line for convenience which does not change the conclusions in the following discussions. The solid and dotted arrow lines indicate the annealing direction and the relaxing direction (refer to the Sec. III B), respectively. The phase diagram can be divided into three regions as indicated in Fig. 3. Region I has lower bulk T_c with a broader transition, this is just the disadvantage of the dynamic annealing method as a nonequilibrium process. Region II covers the transition from UA to OA regime including the optimal-annealing regime. In this region, the superconducting transition width can be tuned to be very sharp by optimizing the annealing temperature and duration. Moreover, the superconducting volume keeps being constant in the whole region thus the following sections in this paper will be focused on this high-quality single-phase region. In region III, it was difficult to get a single phase with T_c lower than 18 K. Instead, the sample became inhomogeneous and was often separated into two (or more) phases, the open circles in Fig. 3 indicate the respective T_c values of two superconducting phases coexisting in one sample. Nevertheless, it should be worth trying some new procedures in future to get a single phase with lower T_c in the OA regime.

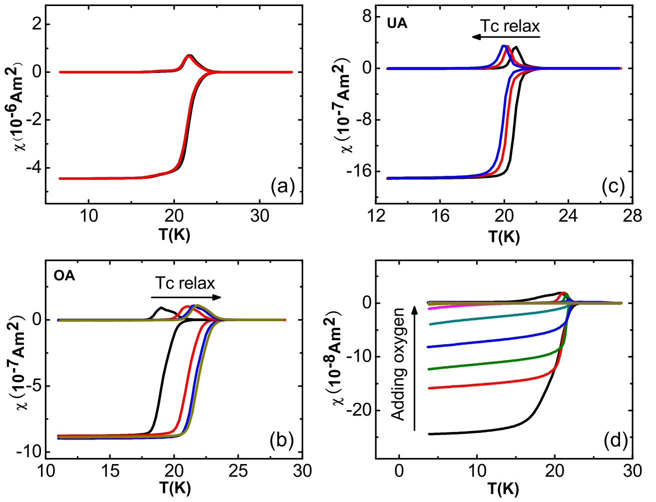

FIG. 4. (Color online) (a) Superconducting transitions of the same sample measured at two different times with an interval of almost ten months. [(b) and (c)] T_c relaxations at OA and UA regimes, respectively. (d) Oxygenated process in atmosphere.

B. T_c relaxation

The bulk superconductivity of PLCCO single crystal is very stable in usual conditions. As shown in Fig. 4(a), an annealed sample was kept for ten months and there was no any change in its T_c value. However, a remarkable find in this work is that T_c will increase at room temperature after the sample is annealed to OA regime followed by a rapid quench to below 200 °C within three minutes, which is not necessary for the processes shown in Figs. 2 and 3. As shown in Fig. 4(b), T_c was 19.0 K in the beginning, then increased to 21.1 K after nine days and went up to 21.5 K after another 18 days, finally, it became 21.8 K after another 37 days. The T_c relaxation was also found in UA regime but it was much weaker than that in OA regime and T_c decreases with the lapse of time in this case. As shown in Fig. 4(c), T_c was 20.7 K in the beginning, then decreased to 20.2 K after 80 days and finally went down to 20.0 K after another 114 days. In both UA and OA regimes, T_c relaxation tends to be saturated ultimately.

T_c relaxation in atmosphere at room temperature has also been found in hole-doped cuprates such as YBCO,[22,23] which was proved to be related to oxygen-doping effect. However, the situation of PLCCO seems different. The superconducting transition revealed by ac susceptibility shown in Figs. 4(b) and 4(c) moves parallel with an almost identical transition width and superconducting volume, which indicates that T_c relaxation is a bulk behavior. Quite the contrary, the oxygenated process we can successfully applied on PLCCO at 400 °C in atmosphere is not a bulk behavior. As shown in Fig. 4(d), with oxygen injecting, more and more portion of the sample is fully oxidated and hence became nonsuperconducting while less and less portion, unaffected by oxygen, almost keeps it's original T_c value. Thus the superconductivity volume decreases rapidly. Therefore, the T_c relaxation observed here cannot be related to oxygen doping.

In order to get further insight into this point, we cut one sample, annealed to OA regime with quenching procedure,

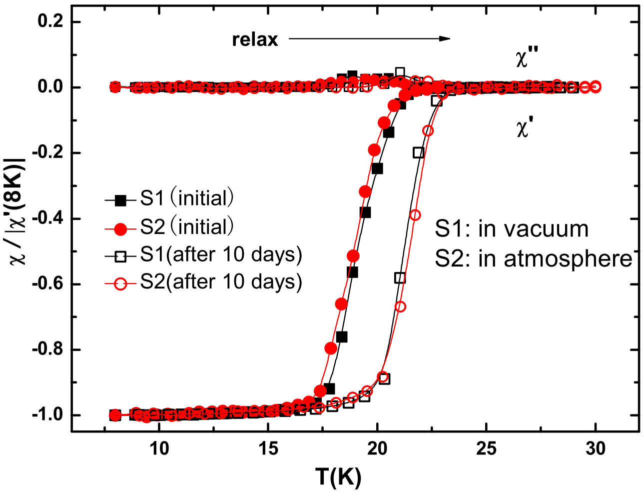

FIG. 5. (Color online) T_c relaxations in OA regime. Samples S1 and S2 were cut from the same sample and stored in vacuum and atmosphere, respectively. The curves are normalized for comparing.

into two pieces (S1 and S2). Then S1 was kept in high vacuum to prevent oxygen from injecting into the sample while S2 was kept in atmosphere for comparing. It can be seen clearly in Fig. 5 the effect of T_c relaxation is almost identical for both samples, indicating that the T_c relaxation observed here should be caused by oxygen rearrangement inside the sample instead of a change in oxygen concentration.

C. Mechanism of OA regime and T_c relaxation

The T_c evolution with oxygen reduction, as shown in Fig. 3, seems to be very similar to the doping effect by substituting tetravalent elements for trivalent ones. However, many experiments have ruled out the doping effect as the origin of such T_c evolution in electron-doped cuprates. Nevertheless, the real role of oxygen reduction is still in debate and one of the controversies is the contribution of O(1) and O(3). Some experiments supported that the slight amounts of O(3) causes disorder and impurity scattering, and the O(3) removal is responsible for the appearance of superconductivity.[3,4,6,7,16,17] On the contrary, some other results suggested that the oxygen vacancies created by O(1) removal in CuO_2 plane could suppress the strength of long-range AF correlations, which enables the emergence of superconductivity.[8,12,20,21] According to the appearance of an epitaxially grown impurity phase of cubic $(RE,Ce)_2O_3$ after oxygen reduction,[9,11,24,28] a microscopic picture was proposed most recently,[24] demonstrating that in as-grown samples there are some Cu deficiencies, oxygen removal in CuO_2 plane can repair these Cu deficiencies, which effectively reduces the disorder and provides itinerant carriers, thus induces superconductivity. Although all the scenarios mentioned above can successfully explain the appearance of superconductivity and the T_c increasing with oxygen removal in UA regime, none of these can explain the T_c decrease in OA regime revealed in this work, thus there should be some other mechanism of the oxygen reduction in OA regime.

According to the data of neutron-scattering and thermogravimetric analysis,[24] based on the same sample as ours, O(2) and O(3) [if O(3) does exist in the samples] are hardly to be removed from PLCCO single crystals. Moreover, by previous understanding on some other electron-doped cuprates,[3,4,6,7,16,17] O(3) removal always increases the T_c by reducing impurity scattering. Thus we can conclude that the O(1) removal from CuO_2 plane should be responsible for the T_c decrease in OA regime. Although it has been suggested that in UA regime O(1) vacancies in CuO_2 plane suppressed the long-range AF correlations and thus enhanced the superconductivity,[8,12,20,21] our experiment present a strong evidence that in OA regime impurity scattering or disorder effect of O(1) vacancies becomes dominant over the other effects (including that of suppressing AF correlations) and thus impairs superconductivity. This spontaneously explains the T_c relaxation observed in this work.

According to the discussions in the foregoing section, T_c relaxation in PLCCO is due to a redistribution of the oxygen atoms in the sample, thus there should be some metastable sites of oxygen in the just quenched sample. The PLCCO sample is very stable [see Fig. 4(a)] and hence the atoms in the intrinsic sites of O(1) and O(2) could not be mobile at room temperature. As mentioned above, in OA regime the oxygen reduction mainly removes the oxygen in CuO_2 plane. In the process of being extracted from the CuO_2 plane to the outside of the material, the atoms of O(1) have to pass through the interstitial sites. When the sample is quenched rapidly from a high annealing temperature to a low temperature, some oxygen atoms will temporarily settle in the metastable interstitial sites. Thus at room temperature these oxygen atoms will return back to the CuO_2 planes gradually over time due to chemical potential or lattice stress. This process will repair the impurities and disorders in CuO_2 planes and enhance T_c value. Therefore, in OA regime, the T_c relaxation possesses the same mechanism as that of annealing procedure. On the other hand, for the relaxation in UA regime, T_c decays with time which is opposite to the case of OA regime (as shown in Fig. 4). This indicates that restoration of O(1) indeed boosts AF correlations in PLCCO as suggested in Refs. 8 and 14, which is dominant over the impurity/disorder effect in UA regime and thus leads to a decreasing T_c relaxation.

Since such enhancement of AF correlations indeed exists, it is possible to be detected even in OA regime though it does not play a dominant role in this case. For this purpose, the temperature dependence of resistivity ρ and Hall coefficient R_H in OA regime are strongly desired. Since the exact values of ρ and R_H are closely related to the sample quality,[3] to obtain the intrinsic variation in the properties of the samples, it is necessary to do the experiments on the same crystal. The T_c relaxation observed here supplies an uncommon way to measure ρ and R_H on the same sample. In our experiment, a sample was annealed to the OA regime followed by a quenching procedure and was measured immediately. Then the sample was kept on the sample holder for ten days before it was measured again. In the measurements, even the electrodes need not to be refabricated, allowing a precisely detection of the change in ρ and R_H from the prerelaxation state to the postrelaxation state. As shown in Figs. 6(a) and 6(b), a

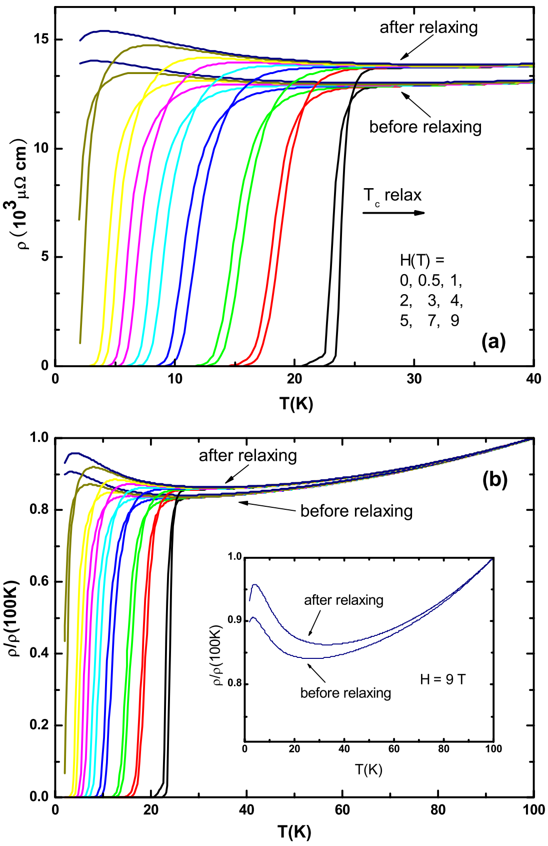

FIG. 6. (Color online) Change in resistivity ρ accompanied by the T_c relaxation in the OA regime. (a) Temperature dependence of resistivity at various fields before and after relaxation. (b) The normalized resistivity by the value of 100 K, the inset shows the data of 9 T.

low-temperature upturn appears in the normal-state resistivity for both cases when superconductivity is suppressed by an applied magnetic field, which is consistent with the previous results of NCCO thin films.[4] Moreover, T_c increases from the prerelaxation state to the postrelaxation state, which can be naturally attributed to the fact that the return of the interstitial oxygen to the CuO_2 planes will repair the disorder and reduce impurities in this superconducting layer. Correspondingly, a smaller resistivity accompanied by a weaker low-temperature upturn in R-T curve is expected to be induced by the relaxation. Surprisingly, the experiment gives a totally different result, i.e., the resistivity becomes larger [as shown in Fig. 6(a)] and the low-temperature resistive upturn is enhanced [as shown in Fig. 6(b) and see clearly in the inset] after the relaxation. Information is thus obtained from this seeming inconsistency that the resistive upturn observed here must be dominated by some mechanism other than the disorder effect and/or impurity scattering in CuO_2 planes, such as the spin scattering of AF correlations.[29]

Some theories have predicted that AF correlations will affect the electronic structure of electron-doped cuprates,[30,31] which can be detected by Hall-coefficient measurements. The insets of Fig. 7 show the magnetic field dependence of Hall resistivity ρ_{xy} at various temperatures, here ρ_{xy} was taken as $[\rho_{(+H)}-\rho_{(-H)}]/2$ to eliminate the misalignment effect of the Hall electrodes. It is found that the value of ρ_{xy} changes from positive to negative with increasing temperature from 25 to 90 K and thus the sign of Hall coefficient $R_H=\rho_{xy}/H$ changes correspondingly, as shown in Fig. 7. Most interestingly, the exact temperature where the sign change occurs became lower after relaxation. The sign change in R_H indicates a multiband property with two types of carriers, i.e., electrons and holes in the sample.[4,8] A theoretical work based on the cluster perturbation theory[30] indicated that in electron-doped cuprates the holelike quasiparticle excitations around $(\pi/2,\pi/2)$ in the momentum space are sensitive to the strength of AF correlations. Consequently, when AF correlations are enhanced, the mobility of the holes will be impaired. In this sense, the impaired contribution of the holes after relaxation as shown in Fig. 7 indicates the enhancement of AF correlations (AF fluctuation is most possible here[32,33]), which leads to an increase in spin scattering. This scenario can successfully explain the enhanced low-temperature resistive upturn due to relaxation as shown in Fig. 6. Therefore, the enhancement of AF correlations due to O(1) restoration does extend to OA regime as expected by above discussions. Thus oxygen vacancies in CuO_2 plane both suppresses AF correlations and induces disorder/impurity scattering.

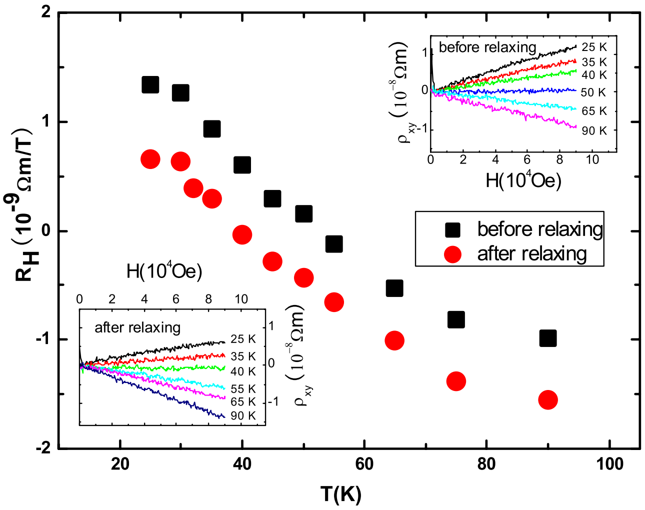

FIG. 7. (Color online) Change in Temperature dependence of Hall coefficient R_H accompanied by the T_c relaxation in the OA regime. The insets show the field dependence of Hall resistivity ρ_{xy} at various temperatures before and after relaxation, respectively.

D. An universal picture of T_c variation in annealing process

According to the T_c relaxation observed here, it has been demonstrated that O(1) vacancies can influence AF correlations and hence the T_c value of PLCCO. Moreover, the strength of AF correlations can play a dominant role in the process of T_c relaxation in UA regime since only O(1) need to be considered. However, if we try to get a comprehensive understanding of the annealing process in UA regime, the Cu vacancies has to be taken into account.[15,24] Though only the amount of oxygen vacancies changes in T_c-relaxation process, it is also accompanied by repair of Cu deficiencies in the vacuum annealing process of PLCCO.[24] Since AF order is built from the Cu-cite spins, repairing Cu vacancies should be more efficient to boost AF correlations against the negative effect from the oxygen vacancies in the oxygen-reduction process. In this sense, instead of the strength of AF correlations, Cu-vacancies-induced impurity/disorder effect should be responsible for the T_c increase in UA regime of PLCCO since the amount of the repaired Cu deficiencies is almost the same as that of the oxygen vacancies created.[24] Therefore, although there are various factors affecting superconductivity of electron-doped cuprates, which one is dominant depends on the practical situation of the samples. In PLCCO single crystals, the concentration of impurities/disorders in CuO_2 planes determines T_c value, though the strength of AF correlations should also be taken into account. In this picture, Cu vacancies and O(1) vacancies play the dominant role in UA and OA regime, respectively.

Actually, it has been realized long time ago that CuO_2 plane is the key unit for superconductivity. But the issue how the disorder in CuO_2 plane affects the bulk superconductivity is still not settled, though it is very important for understanding the mechanism of HTSC. It has been demonstrated that disorders or impurities on Cu sites may suppress or even destroy superconductivity of HTSC (Refs. 15, 24, 34, and 35) while the effect of O-sites disorder in CuO_2 plane is much more difficult to be studied since the process of manipulating oxygen content in CuO_2 plane is always hindered or accompanied by some other effects. In this work, the effect of O-site disorder in CuO_2 plane can be studied separately in PLCCO single crystals, which should be an important supplement for understanding the mechanism of HTSC. In our previous tunneling experiments,[36] T_c and superconducting gap almost have a linear relationship. Combining these results we could reveal an important fact that a very small number of impurities/disorders at either Cu site or O site in CuO_2 plane leads to a serious depairing effect and thus suppresses T_c, which should be helpful to understand the pairing mechanism of HTSC.

IV. CONCLUSIONS

In summary, using high-vacuum annealing treatment, we have successfully driven the bulk T_c of $Pr_{0.88}LaCe_{0.12}CuO_{4\pm\delta}$ single crystals to an OA regime in which T_c is continuously suppressed with oxygen reduction. A remarkable T_c relaxation was observed at room temperature, which was proved to be caused by the rearrangement of the oxygen atoms inside the samples. In combination with the previous studies, we conclude that a very small number of disorders in CuO_2 planes, no matter on Cu sites or O sites, can lead to a serious depairing effect and thus suppress T_c of $Pr_{0.88}LaCe_{0.12}CuO_{4\pm\delta}$. These results shed light on the physics of CuO_2-plane disorder in cuprates and is helpful to build an appropriate model for HTSC.

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