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Coexistence of ferromagnetism and superconductivity in Cu-rich lanthanum Cu-oxides

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Abstract. We have measured the zero field and field cooled magnetization of the lightly oxygen doped Cu-rich $La_2CuO_{4+\delta}$ in a wide temperature range (5 K to 350 K). The data together with the evolution of the magnetic hysteresis loop suggest that the ferromagnetism with Curie temperature of 280 K coexists with superconductivity below the transition temperature $\sim$ 34 K. The coexistence occurs in the hole-rich clusters of size $\leq$ 150 nm, which are electronic phase separated from the hole-poor antiferromagnetic background.

PACS. 74.72.Dn La-based cuprates – 74.25.Ha Magnetic properties – 74.90.+n Other topics in superconductivity

1 Introduction

The interplay of superconductivity (SC) and magnetism has been an interesting topic for decades. In a spin singlet superconductor, the electrons form a condensate of Cooper pairs with antiparallel spins, and the SC is compatible with antiferromagnetism (AFM). The ferromagnetism (FM) is compatible with the spin triplet SC in analogy to the superfluidity in liquid helium-3. Very recently, coexistence of SC and FM was observed in UGe_2 [1] and $ZrZn_2$ [2], where the SC is believed to be spin triplet [3,4].

FM and the spin singlet SC are not compatible, since the FM polarizes electron spins hence breaks the Cooper pairs. However, in the presence of magnetic impurities, electron spins of a superconducting state may be partially polarized to gain the exchange energy leading to the coexistence of FM and SC. Nevertheless, it is difficult to observe the coexistence in experiments because it costs an energy, $\sim$ the superconducting gap, to break a Cooper pair [5,6]. The high temperature SC [7–11] is different. It has a d-wave symmetry with gapless excitations in nodes, so that electron spins may be polarized with little cost in energy. This should provide a possible candidate to observe and to study the coexistence of FM and SC and their competition.

In this paper, we report the coexistence of SC and FM and their competition in Cu-rich $La_2CuO_{4+\delta}$ with lightly excess oxygen concentration δ. The samples are electronic phase separated ones with superconducting hole-rich clusters embeded in the hole-poor antiferromagnetic (AFM) background. We have measured their magnetization in the field cooling (FC) and zero field cooling (ZFC) cases in a wide temperature range and the magnetic hysteresis loop. The sample becomes ferromagnetic at a Curie temperature $T = T_0 \sim 280$ K, and superconducting at $T = T_C \sim 34$ K. Both the hysteresis loop and the FC and ZFC magnetization data show that the FM persists well below T_C, and coexists and competes with the SC. We have verified that both FM and SC occur in the hole-rich clusters.

2 Experiments

The Cu-rich $La_2CuO_{4+\delta}$ samples were prepared using conventional solid reaction method [12]. Their atomic nominal composition is $La : Cu = 2 : 1 + x$, with $0 \leq x \leq 0.18$. The sample without the extra oxygen ($\delta = 0$) is AFM ordered, and has a Néel temperature of $T_N \approx 320$ K (as

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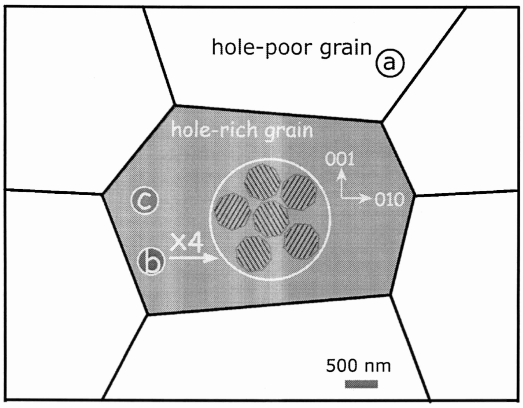

Fig. 1. A schematic image of Cu-rich La_2CuO_4 grains with different hole densities. Hole poor grain a: lowest density; hole-rich grain c: higher density; hole-rich cluster b: highest density. The aperture diameter used in selecting the observed area is $\leq 150 - 500$ nm.

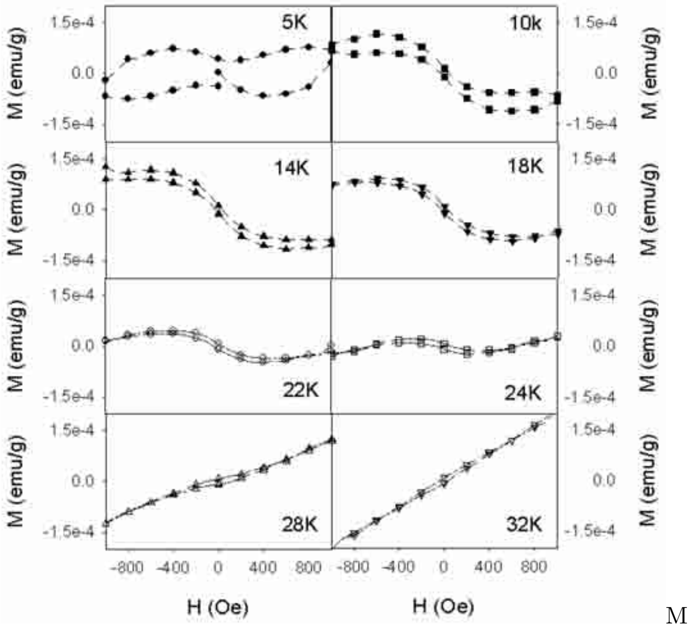

Fig. 2. Hysteresis loops for Cu-rich $La_2CuO_{4.003}$ with La:Cu $\sim 2 : 1.06$ at various temperatures from 32 K (near T_{SC}) to 5 K.

shown in Fig. 3b), which is $\sim$ 30 K higher than that in the stoichiometric La_2CuO_4. We have performed X-ray diffraction, transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS) to examine the microstructure and charge distribution of the sample. The data obtained from all these measurements show that the excess Cu atoms are distributed homogeneously within the sample and enter the La_2CuO_4 lattice. The sample is single-phased and composed of grains with sizes about 5–6 micrometers [13–15]. Each grain is a perfect Cu-rich single crystal with the phase structure of La_2CuO_4. TEM shows that the samples are essentially impurity free till $x = 0.08$. In samples with larger x, the remaining doped Cu-atoms form CuO impurity phase (but there is no evidence of any other types of impurities). Our experiments indicate that all the essential properties reported here are related to the single $La_2CuO_{4+\delta}$ phase, and are independent of these CuO impurities. Quantitative analyses of the EELS indicate that up to about 5% of La ions are replaced by the doped Cu atoms [14], consistent with the nominal sample composition after extracting the CuO impurities.

In Figure 1, we show a schematic image of the hole distribution of the sample obtained from the EELS spectra. A hole-rich grain (region c in Fig. 1) is phase separated from the sample and surrounded by hole-poor grains. In the hole rich grain, the hole density is also inhomogeneous. The EELS spectra show that within the hole-rich grain there are some hole-rich clusters (region b of Fig. 1) in which the hole density is much higher than the rest part of the grain. Since the grain is a perfect single crystal, the phase separation inside the grain is electronic indeed. The electron diffraction pattern shows that the holes in the hole-riched area are modulated ordering [12–15] with a certain modulation vector. The selected area diffraction indicates that when the probed area is of ≥ 200 nm the diffraction pattern has a modulation structure with a characteristic modulation vector $q = 1/4b^* \pm 1/3c^*$ and a modulation period of ~ 18.9 Å [13–15]. As the aperture of electron beam decreases to $\leq$ 150 nm, the single-modulation vector of $1/4b^* + 1/3c^*$ or $1/4b^* - 1/3c^*$ with the same modulation period were observed in the probed area. We thus estimate the size of the hole-rich cluster to be ≤ 150 nm.

Before we describe the magnetic properties of the Cu-rich $La_2CuO_{4+\delta}$, it is useful to briefly recall some of the basic properties of the La_2CuO_4 without the extra Cu-atoms. The parent compound is an antiferromagnetic insulator at low temperatures. The sample becomes superconducting at a transition temperature $T_C \approx 30 - 40$ K when some of La atoms are replaced by Sr or Ca, or when the excess oxygen atoms are introduced, but does not show any FM. Our motivation to study Cu-rich $La_2CuO_{4+\delta}$ is that the substitution of Cu (valence 2+) for La (valence 3+) leads to a spin-1/2 impurity on a replaced La-site. This may enhance the AFM correlation in the neighbouring CuO_2 planes and induce new magnetic structures.

We used a quantum design magnetometer MPMS-V to measure the magnetization and the magnetic hysteresis loop for various samples with $0 \leq x \leq 0.18$. These are the comparative measurements. The measurements were performed on each sample before and after annealing in Ar at 850 °C for 8 hours to expel excess oxygen ($\delta \sim 0$). The sample is electronic phase separated before the annealing, and shows no phase separation after the annealing. FM and SC are only found in the phase separated samples before the annealing. Since the hole-poor region is AFM, we attribute the FM and SC in this compound to the hole-rich clusters (region b in Fig. 1). We have measured the magnetic hysteresis loop, which shows clear signature of FM within the temperature region between ~ 280 K (above $T_N \sim 250$ K) and T_C [16]. Figure 2 shows the hysteresis loops measured in the temperature region

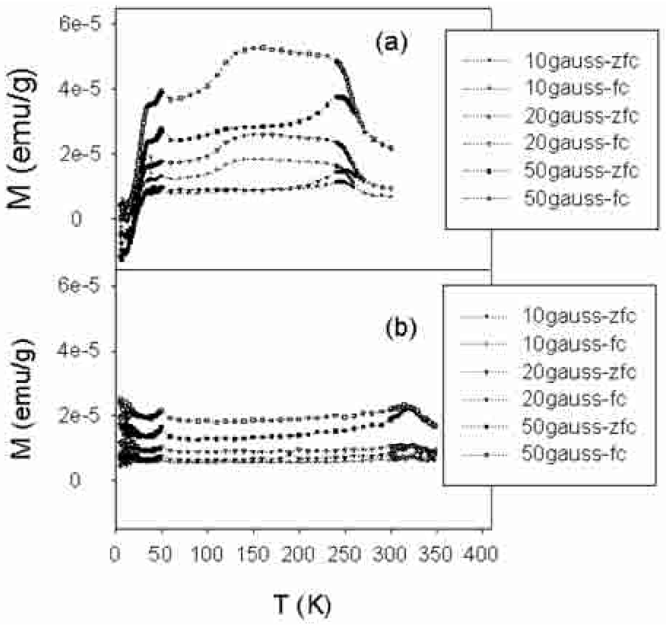

Fig. 3. Magnetization-temperature curves at low magnetic field for phase-separated (a) and non-phase separated (b) Cu-rich cuprate.

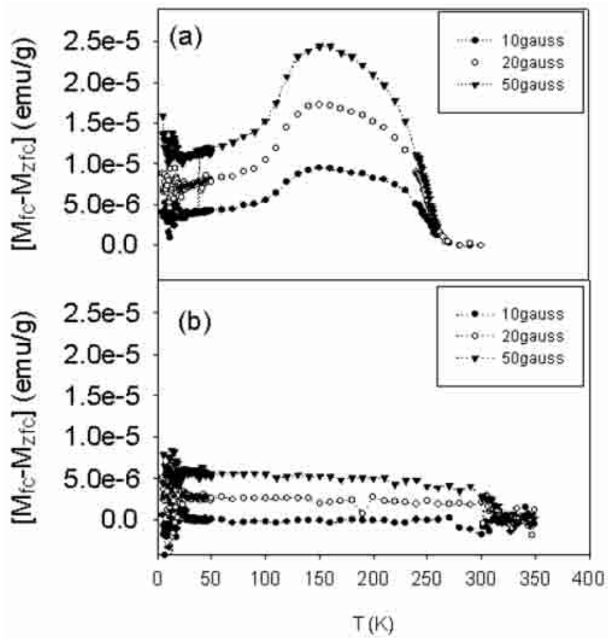

Fig. 4. Temperature and magnetic field dependence of M_{FC}-M_{ZFC} for phase-separated (a) and non-phase separated (b) Cu-rich samples.

extended to below T_C. The hysteresis loops indicate the coexistence and competition of FM and SC for the sample with $x = 0.06$ at temperature ranging from near T_C to 5 K. Within this temperature region, one can see that as temperature decreases, the hysteresis loop changes gradually from FM-like near T_C ($T = 32$ K) to SC-like well below T_C ($T = 5$ K). This unexpected result suggests that the FM persists well into the superconducting state, namely the FM and SC order parameters coexist in the hole-rich clusters. The enhancement of the SC and the relative suppression of the FM with cooling indicate that these two order parameters compete with each other.

We have measured the magnetization of the Cu-rich cuprate in both FC and ZFC cases at various magnetic field $H = 10, 20, 25, 30, 50, 80$, and 1000 Oe. In Figure 3a, we show the temperature dependence of the magnetization of a typical sample with excess oxygen atoms at the magnetic field $H = 10, 20$, and 50 Oe. The magnetization difference between the FC and ZFC cases is plotted in Figure 4a. As one can see from these figures, the ZFC and FC magnetizations are the same at $T > T_0 \sim 280$ K (paramagnetic state), and start to deviate from each other at 280 K. There is a sharp up-turn in the magnetization curve in the temperature region 280–250 K as T decreases. This suggests an onset phase transition of the system into the ferromagnetic state. We have observed this behavior for all the Cu-rich (with various values of x) samples with light excess oxygen. We identify 280 K to be the Curie-Weiss temperature of this system. As T further decreases to below $T_C \sim 34$ K, the system undergoes a superconducting transition as evidenced by the change of the direction of the magnetization curve.

To get more insight, we have analyzed the magnetization data. We denote $M_{\rm dia}$ to be the diamagnetization of the SC, defined as the change of the magnetization in the superconducting transition from T_C-onset to the end. From the experimental data, we obtain $M_{\rm dia}$(FC) and $M_{\rm dia}$(ZFC), corresponding to the diamagnetization in the FC and ZFC cases, respectively. At low fields $H = 10$ and 20 Oe, which are below $H_{c1} \sim 25$ Oe as estimated from the H-M curve in the superconducting state, we found that $M_{\rm dia}$(FC) is almost the same as $M_{\rm dia}$(ZFC). This implies no shielding effect in the Meissner phase and the entire hole-rich cluster is superconducting. Otherwise, we would observe a smaller diamagnetization in the FC case. But for the magnetization, FC and ZFC are different. From Figure 3a and Figure 4a, the difference of the magnetization between the FC and ZFC cases remains below T_C. This suggests that the FM contribution to the magnetization persists during the superconducting transition, consistent with the results of the hysteresis loop.

There are two additional features in the magnetization data to be worthily noted. One is a visible and step-like drop of the FC magnetization as T decreases at ~ 140 K. Though more experiments are needed to fully understand this, we may suggest that the step-like drop in the ferromagnetic magnetization appears to be related to the open of pseudogap, while this temperature ($T \sim 140$ K) is lower than the opening temperature of pseudogap previously suggested in $(La,Sr)_2CuO_{4+\delta}$ system [17]. The formation of the pseudogap around $T \sim 140$ K could suppress the FM and have a drop of FC magnetization around this temperature, a point we will discuss more later. The other feature is the up-turn (10^{-6} emu order) of the magnetization curves at very low temperature region, which is not well understood at this time. Nevertheless, the system in this temperature region remains in the superconducting state.

As a comparison, we show the magnetization data of the *same* sample after the annealing. As we mentioned early, the annealing process expels the excess oxygen in the sample. The annealed sample is not phase seperated and there are no hole-rich clusters, our measurement shows that the hysteresis loops disappear. The magnetization in the FC and ZFC cases are plotted in Figure 3b, and their difference is given in Figure 4b. The main features may be summarized below. (a) There is no SC transition; (b) The magnetization is markedly weaker than that in the phase separated sample and is almost independent of T; (c) The AFM interaction is enhanced resulting in the Néel temperature increases from $\sim$ 250 K (Fig. 3a) to 320 K; (d) The FM is essentially absent or very weak if any. The deviation of the magnetization in the FC and ZFC cases starts at about the Néel temperature $\sim$ 320 K, so the difference of magnetizations in the FC and ZFC cases here may originate from the existed spin canting in the highly ordering AFM background rather than the FM in hole-rich clusters.

3 Discussion

We have established that the FM and SC coexist in the Cu-rich cuprate. Does the coexistence occur in the same region or independently in different regions? While it seems difficult to distinguish directly these two scenarios, we shall argue that the coexistence occurs in the same hole-rich cluster. The most important evidence in support of the first scenario is the absence of FM in the annealed sample without the hole-rich clusters. This shows that the FM is directly related to the charge carriers in the hole-rich clusters. Since these clusters are similar, it is very unlikely that the SC occurs in one cluster and the FM occurs in another cluster. Does the coexsistence be intrinsic in the sense that the spins of electrons in the superconducting state are also polarized? The present experiments do not provide a direct answer to this interesting question. However, the participation of the charge carriers to the FM may imply the polarization. The coexistence we observed in the lightly oxygen doped Cu-rich $La_2CuO_{4+\delta}$ is very different from the coexistence of FM and SC previously reported in $RuSr_2GdCu_2O_{8-\delta}$(Ru-1212) [18]. In that system, the FM occurs in the Ru-O layer, while the SC in the CuO_2 plane was suggested, the two ordering phases seem to be independent in that compound.

The SC in cuprate has been studied intensely, and the SC observed here must be similar in nature. Below we shall propose a mechanism for the observed FM. The extra Cu-ions (Cu^{2+}) are distributed in the La-O plane to form spin-1/2 magnetic impurities. In the hole-rich cluster, there are charge carriers in the CuO_2 plane. The magnetic impurities in the La-O plane interact with the charge carriers in the CuO_2 plane to induce the magnetic interaction or the RKKY interaction among the impurities. This interaction also polarizes the spins of the charge carriers. Therefore, the SC and FM occur in the same region of the sample. The RKKY interaction in a normal metal is well studied [19] and its sign oscillates as a function of $k_F R$, with k_F the Fermi wave vector, and R the distance between the two magnetic impurities. The interaction is ferromagnetic for small k_FR. In the doped cuprate, the electrons are strongly correlated and show many unusual physical properties. The coupling between the impurity and charge carrier has strong dependence on momentum transfer. We speculate these features are in favor of ferromagnetic RKKY interaction, leading to the observed FM. Since the pseudogap should suppress the RKKY interaction, so the step-like drop in the FC magnetization at $T \sim 140$ K may be explained in the theory.

Finally we briefly comment on the coexistence of FM and the d-wave SC. In a d-wave SC, the electrons may be polarized by breaking Cooper pairs with little cost in energy. Therefore, the ferromagnetic order parameter in the d-wave SC must be less suppressed than in the s-wave case. This is consistent with the magnetization measurement reported, where the FM persists well below T_C. In the coexistent phase, the d-wave superconducting transition temperature is also much less suppressed by the FM than in the s-wave one. In the case of weak impurity-electron coupling, theoretical study shows that the suppression of T_C in the d-wave SC is very small [20]. In the present, we observed T_C essentially the same as that in the lanthanum cuprate without excess Cu-atoms. The negligible suppression of T_C is consistent with the d-wave SC of the cuprate.

4 Summary

We have observed coexistence and competition between ferromagnetism and superconductivity in Cu-rich lanthanum cuprate. The magnatization measurements suggest both the ferromagnetism and superocnductivity occur in the hole-rich clusters (with size of $\leq$ 150 nm) of the electronically phase separated sample. Based on d-wave superconductivity, we argued that the coexistence of FM and SC in the present case is likely intrinsic.

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