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Anomalous magnetic and superconducting properties in a Ru-based double perovskite

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Abstract. We have studied the double perovskite [1] structure $Sr_2Y(Ru_{1-x}Cu_x)O_6$ system. The parent compound is an antiferromagnetic insulator with Neel temperature ~ 26 K. Partially substituted the Ru ion by Cu the compounds increase their conductivity drastically and eventually become superconducting. More intriguingly is the observation of the coexistence of superconductivity and magnetic ordering. The superconducting transition temperature T_c and the magnetic ordering temperature T_m are of the same order. The observed magnetic structure and superconductivity of these compounds can be understood in terms of a plausible theoretical model based on the double exchange idea.

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1. Introduction

The common features of the high temperature superconducting cuprates are their parent compounds being antiferromagnetic (AF) insulators and consisting of layered structure with CuO_2 square planes. It has been one major challenge to those who work on superconductivity to search for the possibility of finding new superconductors that contain no CuO_2 planes by proper doping an AF insulating compound. A recent systematic study [2] on the structural stability and superconductivity of the transition-metal doped $YSr_2(Cu_{3-x}M_x)O_y$, particularly for M = Ru, inferred that superconductivity might exist in the compound with $Sr_2Y(Ru_{1-x}Cu_x)O_6$ stoichiometry. The double perovskite compound [3] A_2YRuO_6(2116), where A stands for divalent alkaline earth, is a known antiferromagnetic insulator. We observed superconductivity in this compound system with small amount of Cu-doping, a 50 K superconducting (onset) transition temperature (T_c) as determined by both resistive and magnetic measurements. Detailed structure refinement shows that the Cu-doped compounds have the same crystal symmetry as their parent compound. There exists no component that is related to the known cuprate superconductors including the Ru-based layered cuprates [4] discovered recently.

2. Sample preparation

All compounds investigated were prepared by a solid-state reaction method. Stoichiometric starting powders of $SrCO_3$ (or SrO), Y_2O_3, RuO_2, and CuO were thoroughly mixed, then repeatedly calcined at 1000°C for several days in air in an Al_2O_3 crucible. Subsequently, the product was ground and pressed into a pellet, then sintered at 1390°C in O_2 for 12 h followed by oxygen annealing. Depending on the doping content x the annealing temperature varies from 1330°C–1400°C. The last step was repeated two to three times. Detailed composition analysis using a scanning electron microscope equipped with EDX analyzer identified the particles with 2116 stoichiometry.

3. Results and discussions

Figure 1 displays the high resolution X-ray diffraction pattern of a typical $Sr_2Y(Ru_{1-x}Cu_x)O_6$ compound [5]. Single phase $Sr_2YRu_{1-x}Cu_xO_6$ with orthorhombic structure was obtained. Table 1 lists the structural parameters, for $x = 0$ to $x = 0.1$, determined from Rietveld refinement of x-ray diffraction spectra. The lattice parameters increase with the Cu-content up to $x = 0.1$ as also listed in Table 1. This result suggests the inclusion of the Cu-ions into the lattice. When $x \geq 0.2$, impurity phases appear indicating that the solubility limit of Cu-ions may be below $x < 0.2$. The refinement also yields the best fit, as shown in Fig. 1, of a random sub-lattice [1] with orthorhombic crystal symmetry (space group pbnm). We noted that the lattice parameters for our $x = 0$ sample are slightly larger that those reported [5] in the literature. This is most likely caused by the use of a significantly higher reaction temperature to prepare our samples. The high processing temperature is essential for the observation of superconductivity. Samples prepared at a lower temperature

are found to have the same crystal structure but to be not superconducting. There appears a small peak at $32.2^\circ - 2\theta$ in X-ray diffraction spectra, for $x > 0.2$ samples, that may be associated with the main peak of $YSr_2(Cu_{2.8}Mo_{0.2})O_{7-\delta}$ [6]. Comparing its peak intensity with the strongest peak of the major phase we estimate the impurity phase for $x = 0.2$ to be at most 2% of the bulk. This impurity phase grows with x. For sample with $x = 0.5$, the impurity phase can be as high as 15% of the bulk.

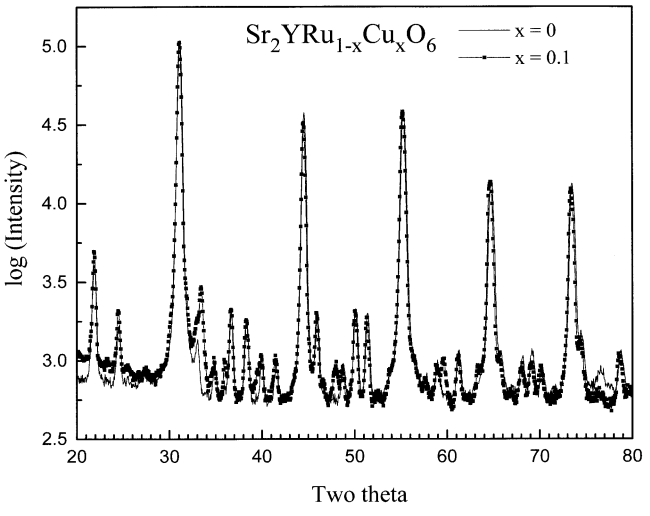

Fig. 1. High resolution x-ray diffraction patterns of $Sr_2YRu_{1-x}Cu_xO_6$, $x = 0$ and 0.1

The resistivity was measured by a standard 4-probe method on sintered bars of $3 \times 4 \times 1$ mm^3. Figure 2 shows the temperature dependence of resistivity for various Cu-dopings. A resistive drop at low temperature appears for samples with $x > 0.03$ and a clear superconducting transition is observed for $x > 0.04$. The resistivity for low-x samples above T_c is semiconductor-like and is considerably higher than those of the cuprates. The onset of the resistive transition typically starts at ~ 60 K and reaches zero-resistance temperature we obtain a phase diagram as shown in Fig. 3. We often observe a small drop in the resistivity at ~ 85 K, for $x \geq 0.1$ samples, preceding the sharp transition at ~ 60 K. It becomes more pronounced with increasing x. For example, our data clearly exhibit two resistive transitions in the $x = 0.3$ sample. This high temperature resistive transition could be related to an impurity phase associated with the Sr-based 123 cuprates. Nevertheless, we were not able to synthesize single phase $YSr_2YCu_{3-x}Ru_xO_{7-\delta}$ by Ru-doping.

The resistivity decrease with increasing Cu doping implies that the concentrations of mobile carriers are

Table 1. Structural parameters of $Sr_2Y(Ru_{1-x}Cu_x)O_6$

Atom	X	Y	Z	$B(A^3)$	Occupancy
$x = 0$; $a = 5.75160(5)$ Å $b = 5.75360(5)$ Å $c = 8.16271(6)$ Å					
Sr	0.0078	− 0.0261 (3)	0.2500	0.85 (3)	2
Y	0.5000	0	0	0.45 (3)	1
Ru	0.5000	0	0	0.45 (3)	1
O1	0.2757	0.2800	− 0.0516	0.57 (3)	4
O3	− 0.0125	0.5143	0.2500	0.57 (3)	2

Space group: pbnm; $R_{wp} = 7.37\%$; $R_p = 5.58\%$

Atom	X	Y	Z	$B(A^3)$	Occupancy
$x = 0.1$; $a = 5.75554(5)$ Å $b = 5.78685(5)$ Å $c = 8.17375(4)$ Å					
Sr	0.0078	− 0.0236 (4)	0.2500	0.79 (4)	2
Y	0.5000	0	0	0.26 (4)	1
Ru	0.5000	0	0	0.26 (4)	0.9
Cu	0.5000	0	0	0.26 (4)	0.1
O1	0.2657	0.2820	− 0.0478	1.09 (4)	4
O3	− 0.0344	0.5068	0.2500	1.09 (4)	2

Space group: pbnm; $R_{wp} = 6.93\%$; $R_p = 5.29\%$

x	a(Å)	b(Å)	c(Å)	V(Å^3)
0	5.75160(5)	5.78360(5)	8.16271(6)	271.5(4)
0.01	5.75314(6)	5.78305(4)	8.16805(5)	271.7(5)
0.02	5.75240(5)	5.78198(4)	8.17095(3)	271.7(7)
0.03	5.75482(4)	5.78525(5)	8.17285(4)	272.0(9)
0.05	5.75512(7)	5.78409(3)	8.17291(5)	272.0(6)
0.1	5.75554(5)	5.78685(5)	8.17375(4)	272.2(4)

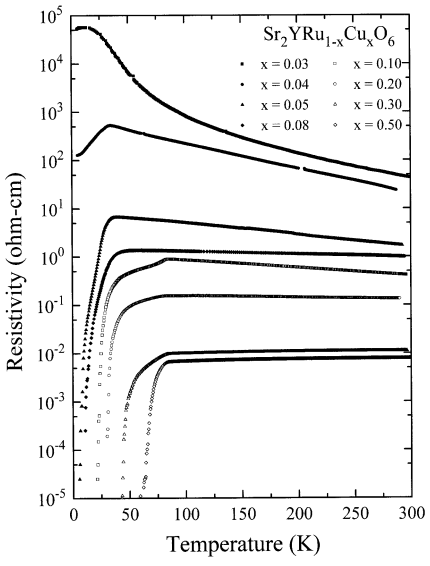

Fig. 2. Temperature dependence of resistivity of $Sr_2Y(Ru_{1-x}\ Cu_x)O_6$

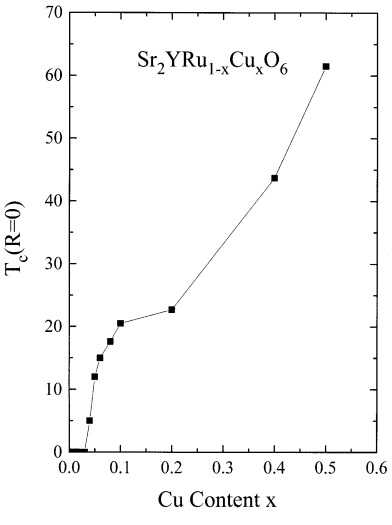

Fig. 3. Phase diagram of $Sr_2YRu_{1-x}Cu_xO_6$. T_c is the zero resistance temperature

related to the Cu doping. The rather broad transition might arise from the imperfection of the sample, but might be also possible due to either the suppression of superconductivity by the magnetic scattering of Ru ions or to an intrinsic microstructure disorder. The magnetic field dependence of $\rho(T)$ is rather complex. Figure 4 displays the upper critical fields determined from the resistive transitions, taking either the temperatures maximum dR/dT or of zero resistance, for an $x = 0.2$ sample measured up to 8 T. The 60 K transition temperature shifts almost linearly to lower temperature at a rate ~ 1 K/T. The zero-resistance temperature first shows similar decrease to that of the 60 K transition but stays almost unchanged for fields higher than 6 T. Choosing the 60 K transition temperature to estimate $B_{c2}(0)$, we obtain

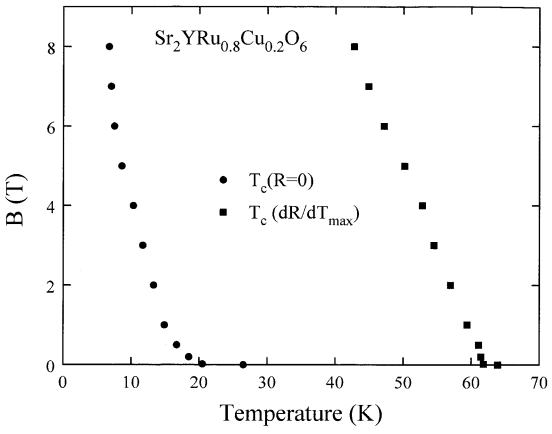

Fig. 4. Field dependence of the transition temperatures for an $x = 0.2$ sample. Solid circles are the zero resistance temperatures and solid squares are the temperatures at which dR/dT is maximum

a value of ~ 50 T using the WHH formula [7]. This value corresponds to a coherence length $\xi \sim 25$ Å. The temperature of the small resistivity drop at ~ 85 K changes only slightly with field. The field dependence of the zero resistance temperature is very much different from those observed in the high T_c cuprates which are governed by the giant flux motion at low temperature. The observed behavior is also not consistent with the picture of strong flux pinning in a conventional 3-d system. This result suggests that the vortex dynamic of Cu-doped 2116 may be intrinsically different from that of the known superconductors.

The magnetic susceptibility was measured by a SQUID magnetometer. The ZFC (zero field cool) and FC (field cool) data for $x \leq 0.1$ and $x \geq 0.2$ samples measured at 10 Gauss are shown in Figs. 5 and 6, respectively. The ZFC curve shows, below ~ 30 K, a relatively weak diamagnetic response that increases with Cu-content. On the other hand, the FC curves exhibit a sharp rise in susceptibility that resembles that of a ferromagnetic transition. In addition, there is a kink at 26 K in both FC and ZFC curves that is similar to the one, due to antiferromagnetic order, as observed in the compound without Cu-doping. This result strongly suggests that antiferromagnetism persists even in the presence of Cu-doping samples. The susceptibility measured at fields higher than 300 G, which is slightly larger than the lower critical field ($B_{c1}(0)$), as determined from the M versus B curves at various temperatures, shows only a positive susceptibility in both after ZFC and FC. However, a sharp susceptibility drop in ZFC and a kink in FC curves are observed. It is noted that the temperature at which the susceptibility exhibits a sharp rise increases slightly with the Cu-content but does not change with the magnetic field. On the other hand, the temperature at which the susceptibility drops decreases slowly with magnetic field. These observations are consistent with the picture of the simultaneous presence of ferromagnetic and antiferromagnetic order as well as superconductivity. The M versus B curve at a fixed temperature, shown in Fig. 7 for an $x = 0.2$ sample, is also consistent with the above picture. From the measured value of $B_{c1}(0)$, the estimated field penetration depth of

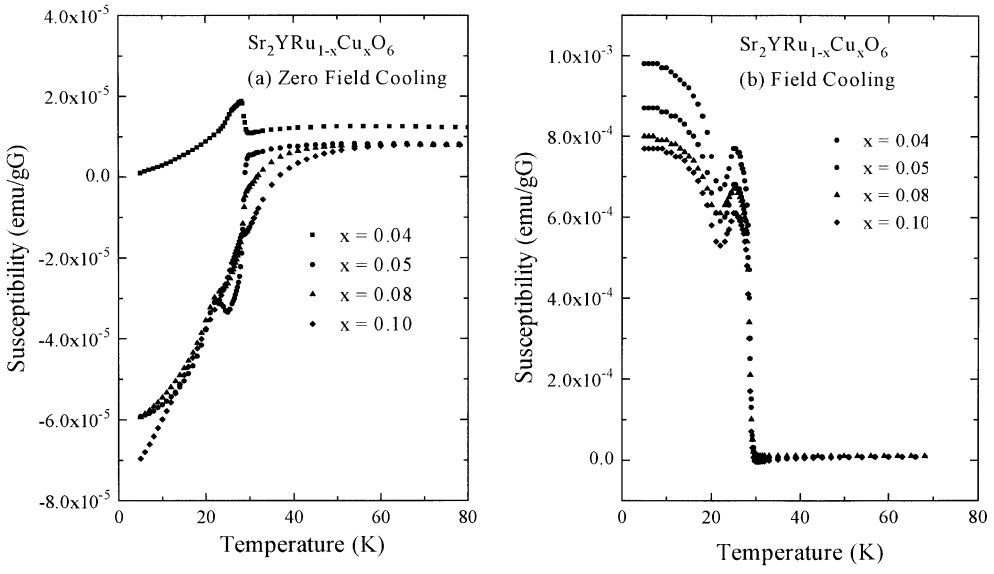

Fig. 5. Temperature dependence of ZFC **a** and FC **b** magnetic susceptibility of $Sr_2YRu_{1-x}Cu_xO_6$ with $x \leq 0.1$

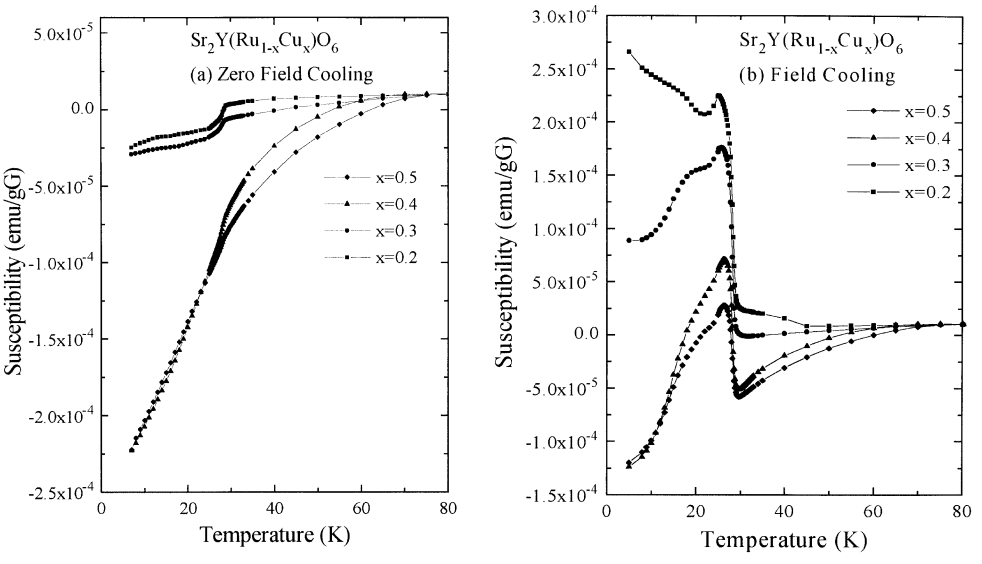

Fig. 6. Temperature dependence of ZFC **a** and FC **b** magnetic susceptibility of $Sr_2YRu_{1-x}Cu_xO_6$ with $x \geq 0.2$

this compound system is about 1500 Å. The relatively small ZFC diamagnetic signals can be understood in terms of the coexistence of ferromagnetic order an superconductivity. It can be shown [8] that in a sample that shows both ferromagnetic order and superconductivity, the true shielding diamagnetic signal will be larger than the difference of the maximum FC magnetic susceptibility and the minimum ZFC susceptibility. Based on this argument, we estimated the minimum superconducting volume fraction to be more than 8% for an $x = 0.04$ sample, suggesting bulk nature of the observed superconductivity.

We have further investigated the pressure effect on the transition temperatures of the samples. Preliminary results show the enhancement of T_c by pressure. However, its effect is only about 50% of the effect on Sr-based 123 cuprates [9]. A preliminary specific heat measurement [10] demonstrates the presence of two pronounced anomalies at 30 K and 26 K that are identical to the temperatures at which magnetic anomalies appear in FC curve. The calculated entropy changes associated with these specific heat jumps are about 5% of $R\ln(2J + 1)$, with $J = 3/2$ for the Ru^{5+} ion, implying a magnetic nature of these two anomalies. The magnetic susceptibility measured at 1 T up to room temperatures shows Curie-Weiss behavior with an effective moment $\sim 4\,\mu B$ (Bohr magneton), that is consistent with Ru in the 5^+ valence state. These results do support the picture of coexistence of ferromagnetism and antiferromagnetism in the sample.

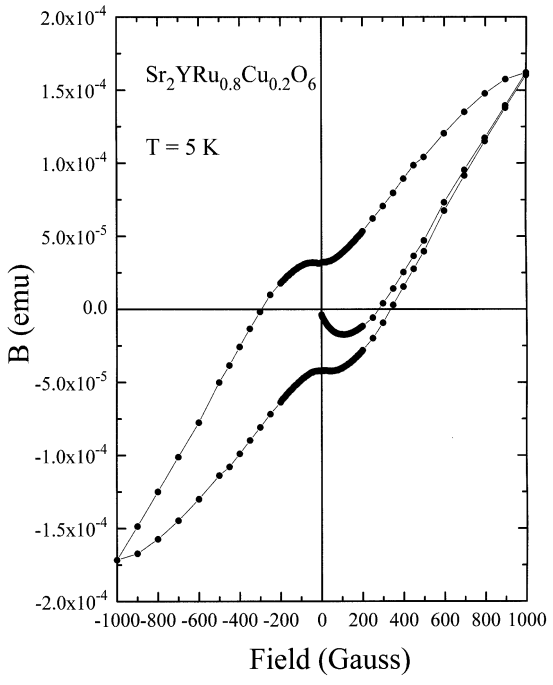

Fig. 7. Magnetic hysteresis of $Sr_2Y(Ru_{0.8}Cu_{0.2})O_6$ measured at 5 K

Detailed results of these measurements will be published elsewhere.

The magnetic properties of the double perovskite Sr_2YRuO_6 have been well studied [3]. The antiferromagnetic order originates from the superexchange among Ru ions that are in $5+$ valence state with a localized moment of total spin $J = 3/2$. Partial doping of the Ru ion by a lower valence Cu ion, likely to be in the $3+$ state, provides mobile holes to the lattice to form a formal Ru^{6+} of spin 1. These holes give rise to "double exchange" [11], similar to the phenomenon in $La_{1-x}Sr_xMnO_3$ compound [12]. The latter has attracted great attention recently due to its interesting colossal magneto-resistance characteristic. The antiferromagnetic spin couplings between Ru^{5+} ions and the double exchange due to the mobile holes result in both ferromagnetic and antiferromagnetic orderings in the magnetic structure according to the theory proposed by de Gennes [13]. It is noteworthy that de Gennes also proposed a superconducting mechanism [14] based on the double exchange and a canted spin state. Based on a more intuitive argument, he suggested that T_c would be in the same order as T_m of the magnetic order. Because of the intrinsic coexistence of the ferromagnetism and superconductivity, we suspect that the Cooper pair may be of odd parity such as the *p*-wave. Whether the observation of superconductivity in $Sr_2Y(Ru_{1-x}Cu_x)O_6$ is the manifest of such a double exchange mechanism remains to be further investigated.

4. Conclusion

In this paper we present evidence of the existence of superconductivity in the Cu-doped $Sr_2Y(Ru_{1-x}Cu_x)O_6$ compounds. There appear two transitions, especially for high Cu-content ($x > 0.3$) samples. The high-temperature phase may likely be associated with the Sr-based 123 compound. However, the data strongly suggest that superconductivity, with $T_c \sim 50$ K, exists in a Ru-based compound which contains no CuO planes. The realization of superconductivity in this Ru-based double perovskite $Sr_2Y(Ru_{1-x}Cu_x)O_6$ is the second example of the Ru-based layered material in addition to the single Ru layer Sr_2RuO_4 [15]. There are several significant features in our observations. First, the T_c of the double perovskite is almost a factor of 40 larger than that of the single layer Sr_2RuO_4. Second, the superconductivity of $Sr_2Y(Ru_{1-x}Cu_x)O_6$, similar to that of the cuprate superconductors, originates from the hole doping to an antiferromagnetic insulator, while Sr_2RuO_4 itself is metallic and becomes superconducting at low temperature without doping. Furthermore, $Sr_2Y(Ru_{1-x}Cu_x)O_6$ is possibly the first example of the coexistence of ferromagnetic order, antiferromagnetic order and superconductivity. Finally, there are more than 300 known oxides that belong to the double perovskite family. This has opened up a complete new venue to the search for high-temperature superconductivity.

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References

1. For a review, please see: Anderson, M.T., Greenwood, K.B., Taylor, G.A., Poppelmeier, K.R.: Prog. Solid State Chem. **22**, 197 (1993)
2. Chen, D.Y., Chien, F.Z., Sheen, S.R., Wu, M.K.: (unpublished); Chen, D.H.: Ph.D. Dissertation, National Tsing Hua University 1995
3. Battle, P.D., Macklin, W.J.: J. Solid State Chem. **52**, 138 (1984)
4. Bauernfeind, L., Widder, W., Braun, H.F.: Physica C **254**, 151 (1995)
5. Battle, P.D., Macklin, W.J.: J. Solid State Chem. **54**, 245 (1984)
6. We have used a sample by mixing in appropriate ratio of $YSr_2(Cu_{2.8}Mo_{0.2})O_{7-\delta}$ and Sr_2YRuO_6 powders as a reference to check whether there is major contribution from Sr-based 123 phase. The reason to choose $YSr_2(Cu_{2.8}Mo_{0.2})O_{7-\delta}$, which has $T_c \sim 40$ K, instead of $YSr_2(Cu_{2.8}Mo_{0.2})O_{7-\delta}$ for the reference sample was that we had difficulty to synthesize single phase $YSr_2(Cu_{2.8}Mo_{0.2})O_{7-\delta}$
7. Werthamer, N.R., Helfand, E., Hohenberg, P.C.: Phys. Rev. **147**, 295 (1966)
8. We assume the ferromagnetic contributions in ZFC and FC to be the same
9. Xiong, Q., Xue, Y.Y., Chu, J.W., Sun, Y.Y., Wang, Y.Q., Hor, P.H., Chu, C.W.: Phys. Rev. B **47**, 11337 (1993)
10. Specific heat measurements were carried out in collaboration with Prof. H.D. Yang and coworkers. The results will be published elsewhere
11. Zener, C.: Phys. Rev. **82**, 403 (1951); Anderson, P.W., Hasegawa, H.: Phys. Rev. **100**, 675 (1995)
12. von Hemholt, R., Wecker, J., Holzapfel, B., Schultz, L., Samwer, K.: Phys. Rev. Lett. **71**, 2331 (1993)
13. de Gennes, P.G.: Phys. Rev. **118**, 141 (1960)
14. de Gennes, P.G.: C.R. Acad. Sci. Paris **305**, 345 (1987)
15. Maeno, Y., Hashimoto, H., Yoshida, K., Nishizaki, S., Fujita, T., Bednorz, J.G., Lichtenberg, L.: Nature **372**, 532 (1994)