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Dramatic increase of paramagnetism before superconductivity quenches in $Y_{1-X}Pr_XBa_2Cu_3O_{7-\delta}$

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ABSTRACT

The samples of $Y_{1-x}Pr_xBa_2Cu_3O_{y-\delta}$ were synthesized with $0 \leqslant X \leqslant 1.0$ and characterized by DC magnetization measurement and X-ray diffraction. The structure of the samples was refined by Rietveld method. The paramagnetism in the samples increases with the increase of Pr dopant. We separate magnetization–temperature curves into two parts, paramagnetic and diamagnetic parts, trying to get more quantifiable analysis. After $X = 0.4$, the percent of paramagnetic part increases dramatically and finally destroys superconductivity. We attribute this dramatic increase of the paramagnetism to structural modulation, especially changes of the chemical bonds (such as: O2–Cu2–O2, O2–Cu2–O4 and O2–O4–O2). The results show that the origin of paramagnetism is strongly related to Cu2 in CuO plane. The relationship between the paramagnetism and superconductivity is discussed based on the experimental results.

1. Introduction

Soon after the discovery of $YBa_2Cu_3O_{7-\delta}$ (Y-123) with T_c above 90 K in 1987, a great deal of interest was concentrated on the elements substitution for different sites in Y-123. Years ago it was demonstrated that $PrBa_2Cu_3O_y$ (PBCO) could not be a superconductor [1], but a semiconductor. Later, some authors [2] reported that PBCO was a good superconductor with the T_c value as high as 80 K. Many people could not repeat this result. Whether PBCO is a superconductor is still under argument. We try to transfer Y-123 to PBCO gradually, studying the detailed change during the transferring, and hope to find some clue to the argument. PBCO is of the same crystalline structure with Y-123 and the study of PBCO is very helpful for the understanding of the mechanism of the high-T_c superconductivity. About the fact that Pr substitution induces the depression of superconductivity, researchers proposed different theories to explain it [3], but no one gain all-pervading acceptance. There will still be a long way in exploring the mechanism of high temperature superconductivity.

In this work, we concentrate on dealing the coexistence of paramagnetism and diamagnetism in $Y_{1-X}Pr_XBa_2Cu_3O_{7-\delta}$ (PY-123) series samples. We found some paramagnetic behavior in the samples, specially when $X > 0.52$. Paramagnetic signal of the samples increases with the increase of Pr dopant, but the pure Y-123 has no such paramagnetic behavior from 10 Oe to 2 T. When comparing the magnetic properties and the change of lattice parameter before and after $X = 0.4$, some interesting results are obtained. The origin of paramagnetic behavior is discussed.

2. Experimental

The series samples of $Y_{1-x}Pr_xBa_2Cu_3O_y$ (X from 0 to 1.0 with interval of 0.05) were prepared by conventional solid-state reaction technique. The raw materials of Y_2O_3, $BaCO_3$, Pr_2O_3, and CuO were ground completely in the proper proportions and calcined at 870 °C for 24 h and at 910 °C for 24 h in air with intermediate grinding. The calcinates were ground and pressed into rectangle pellets and sintered at 930 °C for 24 h, followed by an annealing at 450 °C for 24 h. The last two procedures were completed in a flowing oxygen atmosphere.

The crystalline structures of these samples are characterized by X-ray diffraction (XRD) on a Philips X'pert Pro MPD diffractometer with CuK_α radiation. T_c was determined by DC susceptibility measurement at 10 Oe field from 20 to 120 K, using Quantum Design MPMS system. Detailed structural parameters were obtained by Rietveld refinement. The goodness of fit (GOF = R_{wp}/R_{exp}) of all the samples is about 1.7, demonstrating the refinement results are reliable.

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3. Results and discussion

DC susceptibility and magnetization measurements (zero-field-cooling) for the samples are shown in susceptibility–temperature curves (see Fig. 1). It demonstrates that paramagnetic signal increases monotonically as the dopant increases above superconductivity transition temperature (T_c), while the pure Y-123 sample has completely no paramagnetic signal, even when the field goes up to 2 T. Obviously, it must be the Pr substitution which influences the structure of $YBa_2Cu_3O_{7-\delta}$ and introduces paramagnetism to it.

For the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system, doping makes the change of magnetic property and superconductivity simultaneously. We try to distinguish how much change in the magnetization–temperature (*M*–*T*) curve is induced by paramagnetism and how much by diamagnetism.

We roughly fit the *M*–*T* curves as Curie-Weiss law. The original data are well fitted. The results are shown in Fig. 2 and the sample of $X = 0.52$ is used as an example. Subtracting paramagnetic part fitted by Curie-Weiss Law from the original data, the remaining data is the diamagnetic part, Shown in the insert of Fig. 2. The other samples are dealt in the same way.

From the results shown in Fig. 2, it is found that in the $Y_{1-x}Pr_xBa_2Cu_3O_y$ system, the superconductivity does exist when paramagnetism appears. Separating the susceptibility–temperature curves into paramagnetic part and diamagnetic part, we can clearly see the influence of the paramagnetic part on the superconductivity, which will be shown below.

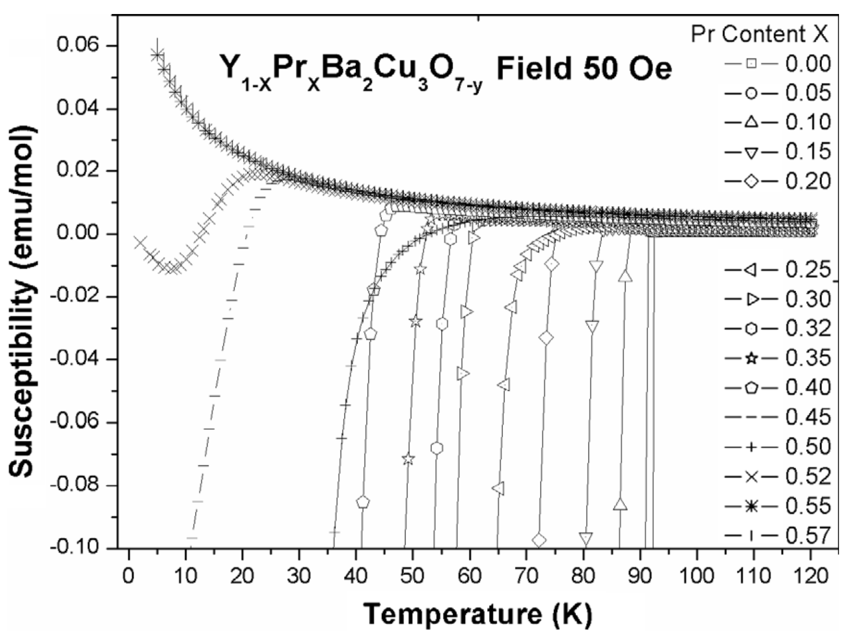

Fig. 1. Susceptibility–temperature (ZFC) curves of $Y_{1-X}Pr_XBa_2Cu_3O_{7-\delta}$ series samples with Pr content range ($0 \leqslant X \leqslant 0.57$, and 1.0).

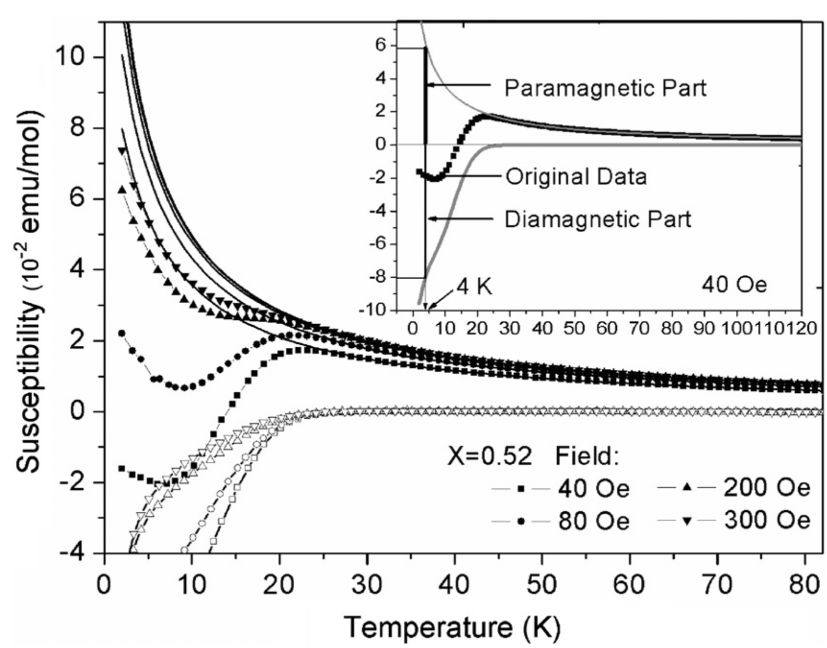

Fig. 2. Susceptibility–temperature (ZFC) curve of $Y_{0.48}Pr_{0.52}Ba_2Cu_3O_{7-\delta}$ sample at different fields. The insert shows the susceptibility–temperature curve at 40 Oe. Fitted diamagnetic part and paramagnetic part are shown. The unit for the susceptibility in the inset is the same as the main figure.

To discuss the influence of the paramagnetic part on the superconductivity, and to get a more quantitative analysis of the relationship among the paramagnetism and Pr doping concentration and superconductivity, the percentage of paramagnetic part at 4 K and the value of T_c versus Pr concentration in the $Y_{1-X}Pr_XBa_2Cu_3O_{7-\delta}$ $(0 \leqslant X \leqslant 0.52)$ series samples are shown in Fig. 3. It is clearly seen as the Pr content increases, the T_c decreases and the percentage of paramagnetic part increases. From the figure, it clearly shows that $X = 0.4$ is a turning point. Before 0.4, the percentage of paramagnetic part increases almost linearly with the Pr content. At the same time, the T_c decreases smoothly with the increase of the Pr content. After 0.4, the paramagnetic part rises dramatically, and the drop of the T_c is also much faster. It is found that the value of T_c has a corresponding relationship with the paramagnetic part in the samples. Kubo et al. [4] once studied the effect of the paramagnetic part on the superconductivity in Tl–Ba–Cu–O system, and they considered that the increase of the paramagnetic part as the decrease of the T_c value is an intrinsic property of the system. Our conclusion is consistent with their consideration, and this phenomenon should be studied further.

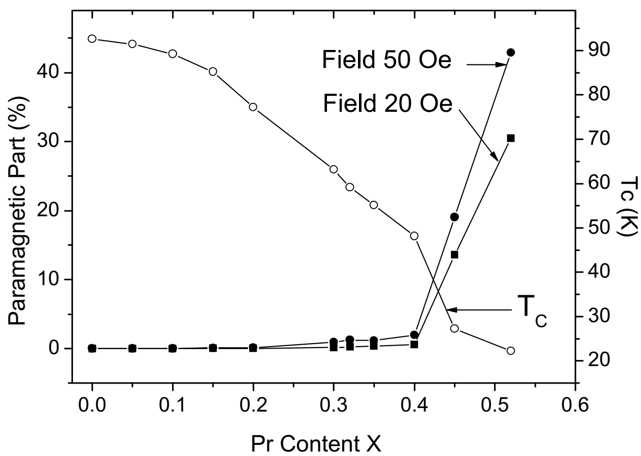

Fig. 3. Percent of paramagnetic part and the value of T_c versus Pr concentration in the $Y_{1-X}Pr_XBa_2Cu_3O_{7-\delta}$ $(0 \leqslant X \leqslant 0.52)$ series samples at 4 K.

The dramatic increase of paramagnetism begins at $X = 0.4$, and when $x = 0.55$, the superconductivity disappears in the $Y_{1-X}Pr_XBa_2Cu_3O_{7-\delta}$ system. We suggest that the much more paramagnetic part in the sample destroys the superconductivity. In order to know the origin of the paramagnetism in the samples, we try to find some clue from crystalline structures. The Rietveld refinements are carried out for all the samples. The GOFs of all the samples is about 1.7, demonstrating the refinement results are reliable. The definitions of a, b, c and atoms in the unit cell are identified in Fig. 4 (insert). The changing trends of these crystalline parameters (a, b, c) are consistent with previous results [5–7], as shown in Fig. 4a. The obvious increase in a and b axes comes from the substitution of Pr for Y, because Pr has ionic radius 1.13 Å but Y 1.02 Å. The c-axis decreases slightly when $X < 0.5$, and slightly increases when $X > 0.5$.

A rather interesting phenomenon is the changes of the chemical bond angles (O2–Cu2–O2, O2–Cu2–O4, and O2–O4–O2) in the crystalline structures, shown in Fig. 4(B–D). These chemical bonds

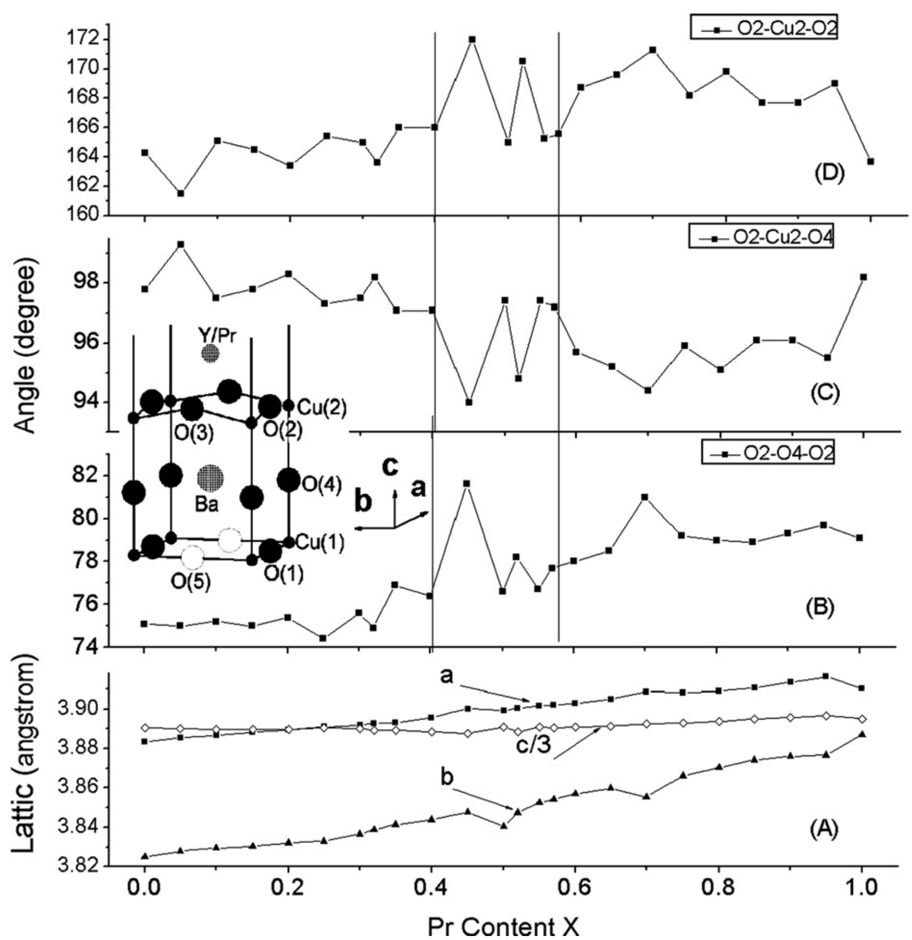

Fig. 4. Crystalline lattice parameters versus Pr content. And chemical bond angle of O2–Cu2–O2, O2–Cu2–O4, and O2–O4–O2 versus Pr content in the samples. The insert is the crystalline structure of $Y_{1-x}Pr_xBa_2Cu_3O_{y-\delta}$.

are closely related with the Cu(2)–O plane and superconductivity. The changes of other chemical bonds are not as obvious as that in Fig. 4. As shown in Fig. 4, the change of the chemical bonds can be roughly divided into three stages according to the x values: 0–0.4, 0.4–0.55, and 0.55–1.0. At the first stage, the change of the chemical bonds with Pr content is relative smooth, and the increase of paramagnetic part also very slow (see Fig. 3). At the second stage, the chemical bounds changes are more significantly, and the paramagnetic part sharply increases (see Fig. 3). At this stage, $x = 0.4$–0.55, the superconductivity of the samples nearly disappears. At the third stage, the change of the chemical bounds tends to smooth again, and the paramagnetic part still sharply increases (no corresponding part in Fig. 3, because the sample becomes non-superconducting in this range). From the results, we suggest that in the $Y_{1-X}Pr_XBa_2Cu_3O_{7-\delta}$ system, as the increase of the Pr content, structurally, the chemical bonds related to Cu(2)–O plane are changed, which may connect with the increase of the paramagnetic part. Finally, the paramagnetic part destroys the superconductivity. The detailed explanation still needs more experimental and theoretic works. From our works above, it is suggested that PBCO should not be a superconductor.

4. Conclusion

The paramagnetism, superconductivity and the structural parameters, chemical bond angle in the $Y_{1-x}Pr_xBa_2Cu_3O_{y-\delta}$ system were investigated. The superconductivity was depressed because of the increase of the paramagnetic part induce by Pr doping. The paramagnetic part increases dramatically from $X = 0.4$ before superconductivity is quenched. The structure parameters, chemical bond angles of O2–Cu2–O2, O2–Cu2–O4, and O2–O4–O2, related with the Cu(2)–O plane, may response the increase of the paramagnetic part in the samples and finally destroy the superconductivity.

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References

[1] C.H. Booth, F. Bridges, J.B. Boyce, T. Claeson, Z.X. Zhao, Phys. Rev. B 49 (1994) 3432.
[2] Z. Zou, J. Ye, K. Kunihiko, Y. Nishihara, Phys. Rev. Lett. 80 (1998) 1074.
[3] Y. Yu, G. Cao, Z. Jiao, Phys. Rev. B59 (1999) 3845.
[4] Y. Kubo, Y. Shimakawa, T. Manako, H. Igarashi, Phys. Rev. B 43 (1991) 7875.
[5] A. Kebede, C.S. Jee, J. Schwegler, J.E. Crow, T. Mihalisin, G.H. Myer, R.E. Salomon, P. Schlottmann, M.V. Kuric, S.H. Bloom, R.P. Guertin, Phys. Rev. B 40 (1989) 4453.
[6] G. Cao, J. Zhang, S. Cao, C. Jing, X. Shen, Int. J. Mod. Phys. B 18 (2004) 3001.
[7] J.D. Jorgensen, Phys. Today 44 (1991) 34.