



Contributions of CuO_2 planes and CuO chains on the transport properties of $\text{YBa}_2\text{Cu}_4\text{O}_8$

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Received 7 September 1998; revised 9 October 1998; accepted 30 November 1998

Abstract

We have investigated the contributions of CuO_2 planes and CuO chains on the transport properties of $\text{YBa}_2\text{Cu}_4\text{O}_8$ by measuring the electrical resistivity and thermoelectric power (S) of $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2(\text{Cu}_{1-y}\text{Zn}_y)_4\text{O}_8$, $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_4\text{O}_8$ and $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_4\text{O}_8$. Pr reduces the mobile carrier concentration in the CuO_2 planes in $\text{YBa}_2\text{Cu}_4\text{O}_8$, as a consequence, the superconducting transition temperature is progressively decreased with increasing Pr. The $S(T)$ data suggest that the metallic behavior at lower temperature of the Pr and Zn doped compounds is contributed by the double CuO chains. On the other hand, the $S(T)$ behavior of Ca doped samples is opposite to that of the Pr doped samples because the doping of Ca in Y-site introduces holes in the CuO_2 planes. However, the substitution of Ga in Cu(1)-site suppresses the carrier concentration in CuO chains and increases the normal-state resistivity revealing the important contribution from CuO chains on the metallic behavior of $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{PrBa}_2\text{Cu}_4\text{O}_8$. © 1999 Published by Elsevier Science B.V. All rights reserved.

Keywords: $(\text{Y}_{1-x}\text{Pr}_x)\text{Ba}_2\text{Cu}_4\text{O}_8$; Thermoelectric power; Cu–O chains; CuO_2 planes

1. Introduction

It is well known that the structure of $\text{YBa}_2\text{Cu}_4\text{O}_8$ (Y124) is closely related to that of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (Y123) and the only difference is that the unit cell of Y124 phase contains double CuO chains instead of a single CuO chain in Y123 [1,2]. On the other hand, although $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ [(Y,Pr)123] series have been studied extensively [3], there are only very few reports on $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_4\text{O}_8$ with $x \leq 0.8$ [4–6] because of unsuccessful synthesis of pure $\text{PrBa}_2\text{Cu}_4\text{O}_8$ (Pr124) at ambient oxygen pressure.

Recently, we have successfully synthesized the whole series of $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_4\text{O}_8$ ($0 \leq x \leq 1$) [(Y,Pr)124] at ambient oxygen pressure and the T_c suppression with Pr is similar to that observed in (Y,Pr)123 [3,7–9]. The x_{cr} (the value of x where the zero resistance temperature disappears) value is larger (~ 0.72) in (Y,Pr)124 than that (~ 0.55) in (Y,Pr)123 [3,9]. It is noted that Horii et al. [10] have reported the synthesis of $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_4\text{O}_8$ system over the entire Pr concentration range $0 \leq x \leq 1$ by hot isostatic pressure (HIP) technique (for $x = 0–0.6$) and the high pressure pure oxygen gas technique (for $x = 0.6–1$). Furthermore, the normal-state resistivity in (Y,Pr)124 remains in the same order of magnitude throughout the whole series in contrast to a metal–

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insulator transition observed in (Y,Pr)123 [3,9]. Thus, it is interesting to investigate how the double CuO chains in (Y,Pr)124 affect the normal-state transport properties and the T_c suppression. Moreover, in order to achieve the better understanding of the roles of CuO₂ planes and CuO chains on the normal-state transport properties, the samples (Y,Pr)Ba₂(Cu,Zn)₄O₈, (Y,Ca)Ba₂Cu₄O₈ and YBa₂(Cu,Ga)₄O₈ are synthesized and studied.

In this paper, special attention is paid to the thermoelectric power (TEP). TEP measurements provide not only information complementary to electrical resistivity, but they are also a more direct probe to the intrinsic properties of polycrystalline materials like these ceramics. In fact, as a zero current measurement, TEP is less sensitive than the electrical resistivity to the grain boundary effects which are always present in granular materials.

2. Experimental

The polycrystalline Y_{1-x}Pr_xBa₂(Cu,Zn)₄O₈, Y_{1-x}Ca_xBa₂Cu₄O₈ and YBa₂(Cu_{1-x}Ga_x)₄O₈ were prepared by the Nitrate Pyrolysis method as described elsewhere [7–9]. All samples were characterised by X-ray diffraction (including low angle) and thermogravimetric analysis. It is found that our sample quality is comparable to those prepared by O₂-HIP technique and high pressure oxygen gas technique [10]. Electrical-resistivity measurements were performed on rectangular specimens cut from sintered pellets employing the standard four-probe technique with silver paint contacts attached to electrical leads. The TEP (S) was measured using the standard dc method with the use of closed cycle cryocooling system. A temperature difference of 1–2° was maintained between the two parallel surfaces of the samples under investigation. To eliminate the effects from the Cu electrodes and reference leads (Cu wires), the absolute thermopower of Cu was subtracted from the measured thermoelectric voltage.

3. Results and discussion

Electrical-resistivity data for Y_{1-x}Pr_xBa₂(Cu_{1-y}Zn_y)₄O₈ ($x = 0-1$; $y = 0$ and 0.02) are

shown in Fig. 1a and b, where the Zn prefers CuO₂ plane [Cu(2)] sites [11]. For $y = 0$, the room temperature resistivity increases with increasing Pr content up to around $x_{cr} \sim 0.7$ and is nearly constant for $x > 0.7$. These are in sharp contrast to those in (Y,Pr)123 where for $x > 0.55$ the normal-state resistivity increases rapidly and a metal–insulator transition occurs. In particular, the metallic behavior of Pr124 is completely different from the semiconducting behavior of Pr123. For Y-rich samples with Zn doping, the normal-state behavior remains metallic, but the resistivity increases and T_c decreases. For example, the resistivity and T_c of Y_{0.8}Pr_{0.2}Ba₂(Cu_{0.98}Zn_{0.02})₄O₈ are similar to those of Y_{0.4}Pr_{0.6}Ba₂Cu₄O₈. While for Pr-rich samples, no significant effect with Zn doping is found. For example, the resistivity of Pr124 is almost identical with PrBa₂(Cu_{0.98}Zn_{0.02})₄O₈. It also deserves to mention that the resistivity slope ($d\rho/dT$) is almost unchanged for both Pr and Zn doping.

Fig. 2 shows the TEP of the (Y,Pr)124 samples with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 . The TEP data of the end members (i.e., $x = 0$ and $x = 1$) of the present investigation are similar to those reported earlier [12–15]. It is found that $x = 0$ compound shows a minimum in TEP at around 140 K. But with

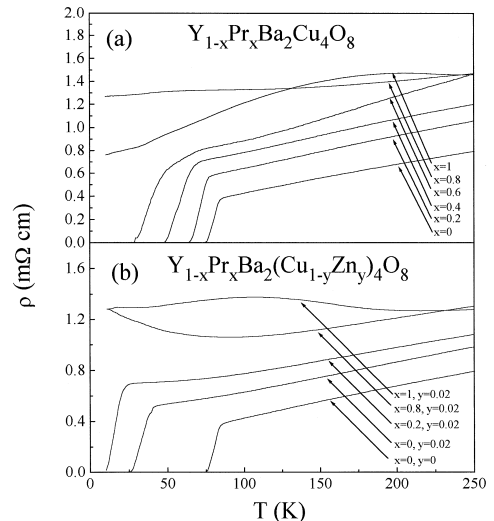


Fig. 1. Temperature variations of electrical resistivity for (a) Y_{1-x}Pr_xBa₂Cu₄O₈ with $x = 0, 0.2, 0.4, 0.6, 0.8$ and 1.0 and (b) for Y_{1-x}Pr_xBa₂(Cu_{1-y}Zn_y)₄O₈ with $x = 0, y = 0$ and 0.02 ; $x = 0.2, y = 0.02$; $x = 0.8, y = 0.02$ and $x = 1.0, y = 0.02$.

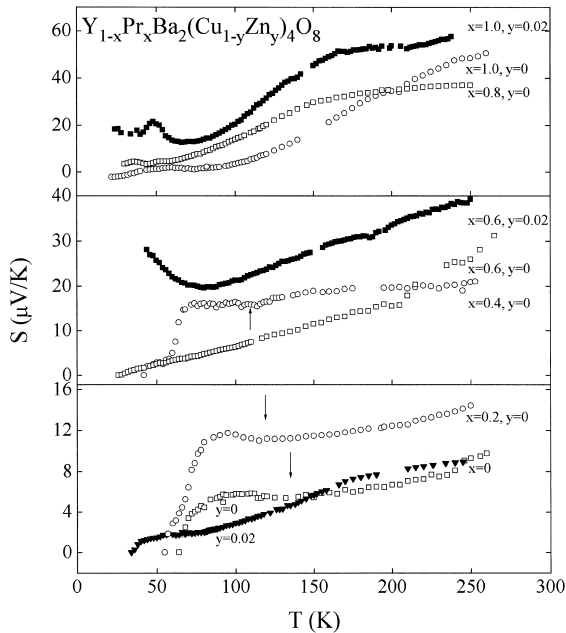


Fig. 2. Temperature variation of thermoelectric power for $Y_{1-x}Pr_xBa_2(Cu_{1-y}Zn_y)_4O_8$ with $x=0, y=0, 0.02$; $x=0.2, y=0$; $x=0.4, y=0$; $x=0.6, y=0, 0.02$; $x=0.8, y=0$; and $x=1.0, y=0, 0.02$. Arrows in the Y-rich samples indicate the temperature where S is a minimum.

increasing x , the minimum in $S(T)$ is shifted towards lower temperature (for $x=0.2$, the temperature is 125 K and for $x=0.4$, it is 115 K). Below the temperature of $S(T)$ minimum, the significant contribution is from CuO_2 plane and above this the significant contribution is from CuO chains. This interpretation is based on the fact the plane contribution to the TEP always has a negative slope, while the slope of the chain contribution is positive [16–19]. For $x=0.6$ sample, S is zero at $T_c \sim 25$ K and increases linearly with temperature up to 200 K. The $S(T)$ slope increases consistently with increase of Pr content for $x > 0.6$. The TEP data for $Y_{1-x}Pr_xBa_2(Cu_{1-y}Zn_y)_4O_8$ with $y=0.02$; $x=0, 0.6$ and 1.0 are also shown in Fig. 2. It is found that for Y-rich samples (for example, $x=0$), the doping of Zn increases the positive slope of the $S(T)$ curve. But for the Pr-rich samples (for example, $x=0.6$ and 1.0) the slope of the $S(T)$ curve is basically unchanged with Zn doping. At low temperature, a sudden upturn is found in the $S(T)$ curve when Zn is doped in Pr-rich (Y,Pr)124.

The transport properties of (Y,Pr)124 can be explained on the basis of the fact that Pr reduces the mobile carrier concentration in the CuO_2 planes and suppresses the T_c . It is found from Figs. 1 and 2 that the effect of Zn on the transport properties of Y124 is similar to that of Pr and the value of $d\rho/dT$ remains the same for the samples with low Pr concentration as well as for the Zn containing samples. Therefore, it seems that Zn reduces/localizes the mobile carrier concentration (although the total carrier concentration may remain the same) in the CuO_2 planes. Also in a very recent paper, it has been suggested that the reduction of T_c in Y124 with Zn doping is due to the localization which is driven by Zn [20]. However, NMR and some other studies indicate that Zn does not alter carrier concentration [21–23]. It has also been explained that Zn reduces T_c by pair-breaking from isotropic scattering with a d-wave order parameter [24]. Therefore, the mechanism of T_c suppression for Zn doped Y124 may not be unique. Though the mobile carrier concentration decreases with Pr substitution the normal-state resistivity remains in the same order which is due to the presence of fully oxygenated double CuO chains. Due to the reduction of mobile carrier concentration in CuO_2 planes with the increase of Pr content, the contributions from CuO chains on the conductivity and TEP become more pronounced. Therefore, with the increase of Pr content, the $S(T)$ minimum is shifted towards lower temperature and TEP rises more rapidly with the increase of temperature which is the characteristic of the CuO chain. The linear increase of TEP for the $x=0.6$ sample clearly indicates the large contributions of CuO chains in the whole temperature range. It is obvious from above discussions that the metallic behavior observed for $x \geq 0.8$ (Fig. 1) even at very low temperature is due to the presence of metallic double CuO chains. The thermopower behavior in the present (Y,Pr)124 differs largely from that of (Y,Pr)123 [25]. The $S(T)$ in (Y,Pr)123 exhibits the typical features of the plane contribution, i.e., an increase of $S(T)$ to a maximum at a temperature and then an almost linear decrease of S towards room temperature [26]. This is due to the fact that (Y,Pr)123 contains poorly conductive single CuO chain in contrast to (Y,Pr)124 which contains fully oxygenated and perfectly ordered double CuO chains. In Y-rich samples, the $S(T)$ slope

increases with Zn doping, but in the Pr-rich samples the slope remains the same due to the fact that the effect of Pr on CuO_2 planes dominates over the effect of Zn. Since the diffusion thermopower and the thermopower due to hopping (if present) approach zero as T tends to zero [27], the rapid increase in S with Zn doping may not be explained unless it has a large contribution from phonon drag effect. In general, with the increase of resistivity, the phonon drag effect decreases [28], which contradicts the present data. Therefore, the actual origin of the $S(T)$ minimum at low temperature (for example, at $T \sim 78$ K for $x = 0.6$; at $T \sim 68$ K for $x = 1$) in the Zn doped (Y,Pr)124 system is not clear. In the high- T_c cuprates, it has been shown that the value of S decreases through the partial substitution of Zn for Cu which is due to the suppression of spin fluctuation or spin correlation [12,29,30]. In the present case, for the (Y,Pr)124 system S increases when Zn is substituted for Cu which may be due to the reduction of plane contribution with Pr doping.

The electrical resistivity and thermoelectric power of $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_4\text{O}_8$ with $x = 0, 0.05$ and 0.1 are shown in Fig. 3. It is found that with the increase of Ca content, the resistivity decreases and T_c increases. It is also found that the $S(T)$ minimum shifts to-

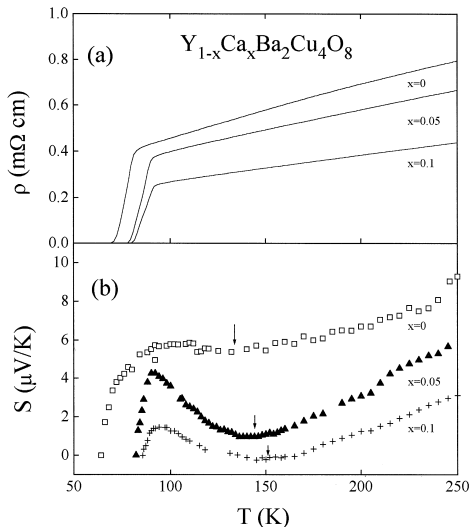


Fig. 3. Temperature variations of (a) electrical resistivity and (b) thermoelectric power for $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_4\text{O}_8$ with $x = 0, 0.05$, and 0.1 . Arrows indicate the temperature where the S value is a minimum.

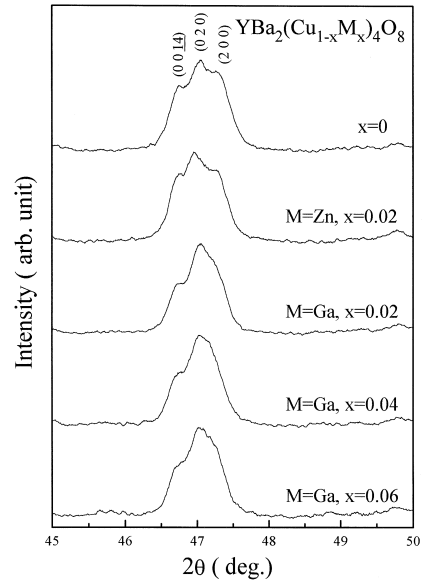


Fig. 4. The X-ray diffraction patterns for $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_4\text{O}_8$ with $x = 0, 0.02, 0.04, 0.06$ and $\text{YBa}_2(\text{Cu}_{0.98}\text{Zn}_{0.02})_4\text{O}_8$ in the range of $45^\circ \leq 2\theta \leq 48^\circ$.

wards higher temperature and the TEP value decreases with the increase of Ca content. These are due to the fact that with the increase of Ca content, hole concentration in the CuO_2 planes increases [31]. This clearly indicates that the effect of transport properties by Ca on the CuO_2 plane is opposite to that by Pr in Y124. Our TEP data of Ca-doped Y124 are consistent with those reported by Tallon et al. [12].

We have also studied the transport properties of $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_4\text{O}_8$ with $x = 0, 0.02, 0.04$ and 0.06 . Fig. 4 shows the X-ray diffraction patterns of these samples in the range $45^\circ \leq 2\theta \leq 50^\circ$. The diffraction peaks of orthorhombic symmetry at (020) (200) are distinguishable in $\text{YBa}_2\text{Cu}_4\text{O}_8$ and $\text{YBa}_2(\text{Cu}_{0.98}\text{Zn}_{0.02})_4\text{O}_8$ but not resolvable in $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_4\text{O}_8$ which are similar to those in $\text{RBa}_2(\text{Cu}_{1-x}\text{M}_x)_3\text{O}_{7-\delta}$ for $\text{R} = \text{Y}$ and Pr ; $\text{M} = \text{Zn}$ and Ga [11,32]. These results may suggest that the Ga substitutes preferentially for the Cu–O chain [Cu(1) site] and changes the crystal structure from orthorhombic to tetragonal whereas Zn is more favorable for CuO_2 plane [Cu(2) site] and the structure remains orthorhombic. The electrical resistivity and TEP data for $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_4\text{O}_8$ are shown in Fig. 5a and b. It is found that with the increase of Ga

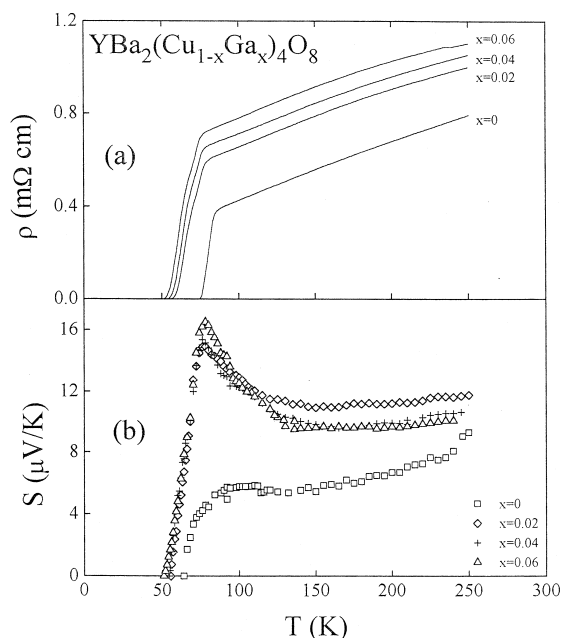


Fig. 5. Temperature variations of (a) electrical resistivity and (b) thermoelectric power for $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_4\text{O}_8$ with $x = 0, 0.02, 0.04$ and 0.06 .

content, the resistivity increases but the suppression of T_c is much smaller than Zn doped case. The change in resistivity can be attributed to a change of the contribution from the Cu–O chains. It is also noted that the increase of resistivity and the decrease of T_c is observed to saturate at $x \geq 0.02$. This may indicate that the solid solution for $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_4\text{O}_8$ is around $x = 0.02$. From the $S(T)$ data, with the increase of Ga content the negative slope ($80 \text{ K} \leq T \leq 200 \text{ K}$) increases. This reveals that with the increase of Ga content the chain contributions decrease and as a consequence, plane contributions become more prominent. Similar effect was observed by Zhou et al. [33] in $(\text{Y}_{1-x}\text{Ca}_x)(\text{Ba}_{2-x}\text{La}_x)\text{Cu}_3\text{O}_{6.96}$ system and by Bernhard and Tallon [26] in $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ system. Therefore, in the present investigation, with the increase of Zn content, the positive $S(T)$ slope increases (we have mentioned above) due to the reduction of plane contribution and with the addition of Ga the negative $S(T)$ slope increases for the reduction of chain contribution.

4. Conclusion

We have studied the resistivity and TEP of polycrystalline $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2(\text{Cu}_{1-y}\text{Zn}_y)_4\text{O}_8$, $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_4\text{O}_8$ and $\text{YBa}_2(\text{Cu}_{1-x}\text{Ga}_x)_4\text{O}_8$ to study the contributions of CuO_2 planes and CuO chains on the transport properties of Y124. The Pr reduces the mobile carrier concentration on the CuO_2 planes. The effect of Zn on the transport properties of Y124 is similar to that of Pr. In contrast, the opposite behavior is found when Ca is doped on Y-site indicating that the Ca introduces holes in the underdoped CuO_2 planes and increases T_c . The substitution of Ga on the Cu(1) site reduces the chain contribution on the transport properties, thus the resistivity increases and the slope of $S(T)$ becomes negative. Therefore, the doping of Pr and Zn makes prominent the chain contribution whereas that of Ca and Ga makes prominent the plane contribution. The TEP data of the present (Y,Pr)124 are different from those of the (Y,Pr)123 [25] due to the presence of metallic double CuO chains in (Y,Pr)124.

Acknowledgements

This work was supported by National Science Council of Republic of China under contract No. NSC87-2112-M110-006.

References

- [1] R.M. Hazen, L.W. Finger, D.E. Morris, Appl. Phys. Lett. 54 (1989) 1057.
- [2] P. Fischer, J. Karpinski, E. Kalidas, F. Jilek, S. Rusiecki, Solid State Commun. 69 (1989) 531.
- [3] H. Radousky, J. Mater. Res. 7 (1992) 1917, and references therein.
- [4] T.H. Meen, Y.C. Chen, M.W. Lin, H.D. Yang, M.F. Tai, Jpn. J. Appl. Phys. 31 (1992) 3825, and references therein.
- [5] M. Kall, A.P. Litvinchuk, P. Berastegui, L.G. Johansson, L. Brojesson, M. Kakihana, M. Osada, Phys. Rev. B 53 (1996) 3590.
- [6] Z. Guo, N. Yamada, K. Gondaira, T. Iri, K. Kohn, Physica C 220 (1994) 41.
- [7] C.W. Lin, J.-Y. Lin, H.D. Yang, T.H. Meen, H.L. Tsay, Y.C. Chen, J.C. Huang, S.R. Sheen, M.K. Wu, Physica C 276 (1997) 225.
- [8] H.D. Yang, J.-Y. Lin, S.S. Weng, C.W. Lin, H.L. Tsay, Y.C.

- Chen, T.H. Meen, T.I. Hsu, H.C. Ku, *Phys. Rev. B* 56 (1997) 14280.
- [9] S.S. Weng, I.P. Hong, C.F. Chang, H.L. Tsay, S. Chatterjee, H.D. Yang, J.-Y. Lin, *Communicated*, 1998.
- [10] S. Horii, Y. Yamada, H. Ikutu, N. Yamada, Y. Kodama, S. Katono, Y. Funahashi, S. Morii, A. Matsushita, T. Matsumoto, I. Hirabayashi, U. Mizutani, *Physica C* 302 (1988) 10.
- [11] T.H. Meen, F.L. Juang, W.J. Huang, Y.C. Chen, K.C. Huang, H.D. Yang, *Physica C* 242 (1995) 373.
- [12] J.L. Tallon, J.R. Cooper, P.S.I.P.N. de Silva, G.V.M. Williams, J.W. Loram, *Phys. Rev. Lett.* 75 (1995) 4114.
- [13] J.-S. Zhou, J.B. Goodenough, *Phys. Rev. B* 53 (1996) R11976.
- [14] J.-S. Zhou, J.B. Goodenough, B. Dabrowski, K. Rogaki, *Phys. Rev. Lett.* 77 (1996) 4253.
- [15] I. Terasaki, N. Seiji, S. Adachi, H. Yamauchi, *Phys. Rev. B* 54 (1996) 11993.
- [16] J.L. Cohn, S.A. Wolf, V. Selvamanickam, K. Salama, *Phys. Rev. Lett.* 66 (1991) 1098.
- [17] J.R. Cooper, S.D. Obertelli, A. Carrington, J.W. Loram, *Phys. Rev. B* 44 (1991) 12086.
- [18] S.D. Obertelli, J.R. Cooper, J.L. Tallon, *Phys. Rev. B* 46 (1992) 14928.
- [19] G.V.M. Williams, M. Staines, J.L. Tallon, R. Meinhold, *Physica C* 258 (1996) 273.
- [20] D.N. Basov, B. Dabrowski, T. Timusk, *Phys. Rev. Lett.* 81 (1998) 2132.
- [21] G.V.M. Williams, J.L. Tallon, R. Meinhold, A. Jánossy, *Phys. Rev. B* 51 (1995) 16503.
- [22] K. Mizuhashi, K. Takenaka, Y. Fukuzumi, S. Uchida, *Phys. Rev. B* 52 (1995) R3884.
- [23] Y. Fukuzumi, K. Mizuhashi, K. Takenaka, S. Uchida, *Phys. Rev. Lett.* 76 (1996) 684.
- [24] J.L. Tallon, C. Bernhard, G.V.M. Williams, J.W. Loram, *Phys. Rev. Lett.* 79 (1997) 5294.
- [25] A.P. Goncalves, I.C. Santos, E.B. Lopes, R.T. Henriques, M. Almedia, *Phys. Rev. B* 37 (1988) 7476.
- [26] C. Bernhard, J.L. Tallon, *Phys. Rev. B* 54 (1996) 10201.
- [27] B. Movaghar, W. Schirmacher, *J. Phys. C* 14 (1981) 859.
- [28] S. Chatterjee, S. Banerjee, B.K. Chaudhuri, N. Froumin, M. Polak, J. Baram, *Phys. Rev. B* 54 (1996) 10143.
- [29] M. Sera, T. Nishikawa, M. Sato, *J. Phys. Soc. Jpn.* 62 (1993) 281.
- [30] J. Takeda, T. Nishikawa, M. Sato, *Physica C* 231 (1994) 293.
- [31] T. Miyatake, S. Gotoh, N. Koshizuka, S. Tanaka, *Nature (London)* 341 (1989) 41.
- [32] H.D. Yang, M.W. Lin, *Phys. Rev. B* 44 (1991) 5384.
- [33] J.-S. Zhou, J.P. Zhou, J.B. Goodenough, J.T. Mcdevitt, *Phys. Rev. B* 51 (1995) 3250.