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High-pressure synthesis and physical properties of ruthenate-cuprates $RuSr_2LnCu_2O_8$ (Ln = Y, Dy, Ho, Er)

T. Kawashima *, E. Takayama-Muromachi

Superconducting Materials Center (Namiki Site), Advanced Materials Lab., National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

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Abstract

We report the series of ruthenate-cuprates $RuSr_2LnCu_2O_8$ (Ru-1212Ln; Ln = Y, Dy, Ho, Er), which were prepared at 1200–1300 °C under 6 GPa. High-purity sample could be obtained for every system with the 'Ru-poor' starting composition, $Ru_{0.9}Sr_2LnCu_2O_{7.8}$. It was confirmed that a solid solution of $(Ru_{1-x}Cu_x)Sr_2YCu_2O_y$ exists and its range terminates at $x \sim 0.1$ without formation of the stoichiometric phase of $RuSr_2YCu_2O_y$. Many Y-based samples were prepared varying the Ru/Cu ratio and the oxygen contents. According to DC susceptibility measurements, ferromagnetism and superconductivity looked to coexist below approximately 40 K in some samples. However, DC resistivity was always quite high even when a sample showed a large diamagnetism in a low temperature region. These results may suggest phase separation regarding the Ru/Cu ratio in the solid solution of $(Ru_{1-x}Cu_x)Sr_2YCu_2O_y$, casting doubt for the coexistence of superconductivity and ferromagnetism.

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1. Introduction

Since the 1212-type compound $RuSr_2GdCu_2O_8$ (Ru-1212Gd) was reported to show coexistence of ferromagnetism and superconductivity below 46 K [1,2], many investigations have been carried out from various points of view [3–30]. One of our interests for this system is whether the Gd-site in Ru-1212Gd can be substituted by other rare earth elements. It is known that larger rare earth elements of Sm and Eu can occupy the Gd-site under ambient pressure [31]. On the other hand, Takagiwa et al. reported that Y-analogue of RuSr₂-YCu₂O₈ becomes stable under high-pressure [32]. Ruiz-Bustos et al. also reported other lanthanides substitution by Ru-1212Gd [28,30]. Namely, high-pressure condition is effective to introduce a smaller rare earth element to the Gd-site.

The Y-phase showed ferromagnetism at 149 K and superconductivity with zero-resistivity at 23 K. However, Meissner effect was not observed by

^{*}Corresponding author. Tel.: +81-29-860-4510/4674; fax: +81-29-860-4674.

E-mail address: kawashima.tetsuya@nims.go.jp (T. Kawa-shima).

DC susceptibility measurement. Moreover, a small amount of impurity phase was included in the sample [33]. The coexistence of superconductivity and ferromagnetism was not, therefore, fully confirmed for this phase.

In the present study, we succeeded to prepare a high-purity Y-based samples under high-pressure and could measure superconducting and ferromagnetic properties for the well-characterized samples. In addition, we synthesized other ruthenate-cuprates $RuSr_2LnCu_2O_8$ (Ln = Dy, Ho, Er) under high-pressure. Their physical properties are also reported.

2. Experimental

Starting materials for high-pressure synthesis were RuO₂ (99.9%), SrO₂, SrCuO₂, Ln₂O₃ (99.9%; Ln = Y, Dy, Ho, Er, Tm, Yb, Lu) and CuO (99.9%). SrCuO₂ was obtained by the conventional solid-state reaction from SrCO₃ (99.9%) and CuO at 1000 °C in air. SrO2 was synthesized through a solution route; H₂O₂ (reagent grade) and NH₃ (reagent grade) were added into a SrCl₂ (reagent grade) aqueous solution, then SrO₂ precipitated was dried at 150 °C in flowing O₂. These materials were mixed in an agate mortar to obtain starting mixtures for high-pressure synthesis. About 300 mg of the mixture was sealed in a gold capsule and allowed to react in a flat-belt-type high-pressure apparatus at 6 GPa, and at 1200-1300 °C for 3 h, then quenched to room temperature. The weight of the gold capsule was checked before and after the high-pressure run. The weight change was always less than 0.2 mg against the sample weight of \sim 300 mg. High $P(O_2)$ HIP treatment was carried out for some selected high-pressure products at 600 °C for 40 h in an atmosphere of approximately 2000 kgf/cm² by the mixture of argon oxygen gas $(Ar:O_2 = 80:20).$

X-ray powder diffraction patterns were obtained by a diffractometer (Philips-PW1800) with Cu K α radiation and lattice constants were determined using the least squares method. DC susceptibility data were collected by a SQUID magnetometer (quantum design, MPMS) at a magnetic field of 1 Oe and in the temperature range from 5 to 200 K by field cooling (FC) and zero field cooling (ZFC) processes. DC electric resistivity was measured by the standard fourprobe method using the physical property measurement system (quantum design, PPMS) in the temperature range from 5 to 300 K. Cation ratios of some selected samples were determined by an EPMA analyzer (JEOL JXA-8600MX).

3. Results and discussion

3.1. $RuSr_2YCu_2O_8$ (Ru-1212Y) phase

For the Ln = Y system, we first tested the ideal starting composition of RuSr₂YCu₂O₈. Since the weight change of a sample was not observed in the process of high-pressure synthesis, net oxygen content of a sample is equal to the initial value in a starting mixture. However such an initial content is not exactly equal to the oxygen content of the Ru-1212Y phase if a high-pressure product is a multi-phase mixture. We tried oxygen content analysis by EPMA, but could not obtain a reasonable value since EPMA is less sensitive for a light element such as oxygen. In this paper, therefore, oxygen content of a 1212 phase is described as a nominal value of a starting mixture. Strictly speaking, it is a synthesis parameter corresponding to the oxygen pressure in the highpressure process, rather than the real oxygen content. However, it would be close to the real oxygen content when a sample is phase pure.

Fig. 1 shows the powder X-ray diffraction patterns of the high-pressure products treated at 1200 °C [sample (A)] and 1300 °C [sample (B)]. Although small peaks attributed to SrRuO₃ and CuO appeared in their X-ray patterns, main peaks could be indexed assuming tetragonal system with a =3.8192(8) Å, c = 11.516(2) Å for sample (A) and a = 3.8168(7) Å, c = 11.522(2) Å for sample (B). The phase-purity was better in sample (A) than in sample (B), suggesting that lower reaction temperature (in this case, 1200 °C) is appropriate to obtain higher phase purity.

According to DC susceptibility data (it is shown in Fig. 3), both samples showed ferromagnetic transitions near 150 K. Diamagnetism was seen for



Fig. 1. Powder X-ray diffraction patterns of the samples having a nominal composition, $RuSr_2YCu_2O_8$. Sample (A) was treated at 1200 °C while sample (B) at 1300 °C. Peaks due to $SrRuO_3$ and CuO are labeled by *.

sample (B) below 39 K both in the FC and ZFC data and it looked large enough to assume bulk superconductivity. On the contrary, only minimal diamagnetism was observed for sample (A) even in the ZFC data. These results suggest that higher reaction temperature (in this case, 1300 °C) is favorable for increasing a volume fraction of the superconducting phase. Ferromagnetism and superconductivity seemed to coexist in sample (B). However, it should be noted that SrRuO₃, which is contained in the both samples as an impurity, has a ferromagnetic transition near 160 K [34]. To see the influence of SrRuO₃, we synthesized SrRuO₃ and measured its DC magnetic susceptibility with the same measuring conditions. The result revealed that about 5% contamination of SrRuO3 can account for the ferromagnetic susceptibilities observed in the samples. The SrRuO₃ contents in the samples (A) and (B) are very roughly estimated to be 1-2% which may not be small enough to be ignored. A SrRuO₃-free sample is, therefore, needed to confirm the magnetic properties of Ru-1212Y.

We carried out many experiments with various synthesis conditions, and a $SrRuO_3$ -free sample was obtained with 'Ru-poor' starting composition at 1200 °C. Fig. 2 indicates the powder X-ray diffraction pattern of the high-pressure product having a nominal composition $Ru_{0.9}Sr_2YCu_2O_{7.8}$ [sample (C)]. Except for a very small peak attrib-



Fig. 2. Powder X-ray diffraction patterns of the samples having a nominal composition, $Ru_{0.9}Sr_2YCu_2O_{7.8}$ [sample (C)] before and after the O₂-HIP treatment.

uted to CuO, all peaks could be indexed by a tetragonal cell with a = 3.817(1), c = 11.500(7) Å (see the pattern denoted as "before HIP-treatment"), and the SrRuO₃ peaks were not observed at all in the pattern even in an enlarged scale. DC susceptibility data of this sample is shown in Fig. 3. Ferromagnetic transition was observed near 150 K as well as in the samples (A) and (B). The magnetic susceptibility at 5 K was slightly (15– 20%) smaller compared with sample (A) which may be attributed to the removal of SrRuO₃. According to these results, we concluded that the ferromagnetism appearing near 150 K is not due to



Fig. 3. DC susceptibility data of the sample (A), sample (B) and sample (C). The arrow part in this figure shows the magnetic transition of Sr_2YRuO_6 .

SrRuO₃ but reflects the magnetism of the Ru-1212Y phase. In this paper, we sometimes deal with samples which was not phase pure, but contained SrRuO₃ with similar percentages to those in the samples (A) and (B). However, according to the aforementioned results, such a small level of contamination does not affect seriously the qualitative discussion given below.

Sample (C) was almost phase pure but did not show large enough diamagnetism to assume bulk superconductivity. Because higher synthesis temperature seems favorable to increase the superconducting volume fraction, we tried a reaction temperature of 1300 °C. In addition, we checked effect of starting oxygen content on the appearance of superconductivity. Fig. 4 shows the powder X-ray diffraction patterns of the high-pressure samples with the nominal composition of Ru_{0.9}- $Sr_2YCu_2O_v$ (v = 7.80-7.95). Small amounts of SrRuO₃ and CuO were included in all samples. The impurity content is minimal for y = 7.80 and increases with increasing the y-value. The lattice parameters, which are shown in Fig. 4, do not change substantially with the variation of the oxygen content. DC susceptibility data of these samples are shown in Fig. 5. The oxygen content has a clear effect on the ferromagnetic transition point near 150 K, i.e., it tends to shift to lower temperature direction with increasing the y-value. Below 37 K, a fairly large Meissner effect, as well as shielding effect, was observed in the high-oxygen-content sample with y = 7.90 [sample (D)].



Fig. 4. Powder X-ray diffraction patterns of the sample having nominal composition, $Ru_{0.9}Sr_2YCu_2O_y$ (y = 7.80-7.95). Peaks due to $SrRuO_3$ and CuO are labeled by *.



Fig. 5. DC susceptibility data of the samples corresponding to Fig. 4.

In the y = 7.95 sample, another ferromagneticlike transition appeared at 27 K under the FC measurement. This anomaly was always observed in high-oxygen-content samples with low phase purities. We assume that the anomaly is ascribed to an unknown ferromagnetic impurity phase although it is not identified yet.

Fig. 6 indicates DC electric resistivity data for the two $Ru_{0.9}Sr_2YCu_2O_y$ samples with y = 7.8[sample (C) in Fig. 2] and y = 7.9 [sample (D) in Fig. 4]. Only minimal diamagnetism was observed in the former sample (Fig. 3) while fairly large one in the latter (Fig. 5). However, both samples showed semiconducting behavior without zero-



Fig. 6. DC resistivity data of sample (C) and sample (D) before and after the O₂-HIP treatment.

resistivity until 5 K. Moreover, resistivity values of both samples were larger by at least three order of magnitude compared with normal-state resistivities of typical cuprate superconductors. For the Ru-1212Gd phase, semiconducting resistivity was also reported before post annealing in oxygen [35]. However, resistivity itself was quite low (about 20 m Ω cm at largest) compared with our samples (about 7 Ω cm at largest). Takagiwa et al. reported that their Ru-1212Y sample showed zero-resistivity after O₂-HIP post-treatment [32]. Lattice parameters of their sample (a = 3.843 Å and c = 11.555 Å) are greatly different from ours suggesting a different cation and/or oxygen composition.

We also tested the HIP treatment with oxygen pressure of 400 atm for sample (C) and sample (D) and the zero-resistivity was indeed attained in the both samples as shown in Fig. 6. However, as shown in Fig. 2 for sample (C), the Ru-1212Y phase was decomposed to Sr_2YRuO_6 and CuO after the HIP treatment. The same decomposition reaction occurred in sample (D), as well. Moreover, Fig. 3 indicates that the superconducting volume fraction did not increase by the HIP treatment. (The anomaly near 27 K in the FC data of the HIP treated sample is due to the magnetic transition of Sr_2YRuO_6 [36].)

The aforementioned experimental data suggest strongly that the samples were inhomogeneous with a mixed state of superconducting and insulating regions and that the decrease of the resistivity after the HIP treatment was due to some physical change in grain boundary. To check this suspicion, we carried out EPMA analysis for sample (C) and sample (D) without the HIP treatment. According to microscope observations, the grain sizes of the samples were 5–10 μ m. We selected about 30 large grains for each sample and analyzed their cation compositions by focusing the electron beam at the center of a grain. The average cation compositions of both samples were roughly identical with the ideal composition of RuSr₂- YCu_2O_{ν} . However, after more careful analysis, it was found that Ru/Cu ratio is distributed in a different way in the two samples. Fig. 7 shows the number of grains observed as a function of the Ru/ Cu ratio. In sample (C), which showed minimal



Fig. 7. EPMA Ru/Cu ratio for sample (C) and sample (D) before the O_2 -HIP treatment.

diamagnetism, the Ru/Cu ratio looks to obey a normal distribution curve around the point of Ru/ Cu ≈ 0.5 . On the other hand, the Ru/Cu ratio distributed more widely in sample (D) for which fairly large diamagnetism was observed. Its distribution histogram suggests existence of Ru-poor grains in the sample and formation of solid solution of (Ru_{1-x}Cu_x)Sr₂YCu₂O₈ [(Ru,Cu)-1212Y] as well as previous reports for Ru-1212Gd and Ru-1212Eu [25,27].

Generally, broadening of (00L) peaks in the powder X-ray diffraction pattern is observed when formation of solid solution is occurred. To investigate the relation of peak width and the physical properties, we checked the peak sharpness and width of (00L) peaks of sample (C) and sample (D). However, we could not detect any difference of peak width between both X-ray diffraction patterns.

In order to confirm the existence of the solid solution, we tested $(Ru_{1-x}Cu_x)Sr_2YCu_2O_{8-x}$ (*x* = 0.1–0.3) nominal compositions, at 6 GPa and 1300 °C. Although we do not show their X-ray patterns here, the phase purities of these samples were quite high and all peaks could be indexed with

tetragonal system. With increasing the Cu content, the *c*-dimension tends to shrink. However degree of the shrinkage is not so high (about 0.01 Å per 10% Cu substitution), and in addition, the *a*-dimension is almost independent of the Cu content. From these results, the presence of the Ru/Cu solid solution was confirmed but it was also found that the deviation of the Ru/Cu ratio from the stoichiometric one is not easily detected by the X-ray diffraction measurement.

As a next step, we examined effect of oxygen content on the phase formation and superconductivity for the samples with x = 0.1 and 0.2. Fig. 8 shows the powder X-ray diffraction patterns of the x = 0.1 samples with y = 7.9-8.1. The phase purity was lower and SrRuO₃ was formed in the high oxygen content samples with y = 8.0 and 8.1. The length of *c*-axis extended with the increase of the oxygen content, which may suggest the introduction of excess interstitial oxygen atoms. DC susceptibility data of these samples are shown in Fig. 9. With increasing the oxygen content, ferromagnetic transition near 150 K shifted to low temperature direction and the magnetic moment due to the ferromagnetism become smaller. Similar tendency was observed in the Ru_{0.9}Sr₂YCu₂O_v samples as described before (see Fig. 5). Under the field-cooling condition, another ferromagnetic-like transition appeared in the y = 8.1 sample. Similar phenomenon was also observed in the Ru_{0.9}Sr₂-



Fig. 8. Powder X-ray diffraction patterns of the sample having nominal compositions, $(Ru_{0.9}Cu_{0.1})Sr_2YCu_2O_y$ (y = 7.9-8.1). Peaks due to SrRuO₃ and CuO are labeled by *.



Fig. 9. DC susceptibility data of the samples corresponding to Fig. 8.



Fig. 10. DC resistivity of the samples corresponding to Fig. 8.

 YCu_2O_y sample with the high oxygen content (see Fig. 5).

Fairly large diamagnetism was observed in the y = 7.9 sample in spite of its small oxygen content. However, zero-resistivity was only observed in the y = 8.1 sample in the DC resistivity measurements as shown in Fig. 10. Normal-state resistivity values were quite high in the three samples, in particular, in the y = 7.9 one. In order to confirm the sample reproducibility, we prepared another y = 7.9 sample with the same synthesis conditions to obtain essentially the same susceptibility and resistivity data.

Fig. 11 shows the powder X-ray diffraction patterns of x = 0.2 samples with y = 7.8-8.1.



Fig. 11. Powder X-ray diffraction patterns of the sample having nominal compositions, $(Ru_{0.8}Cu_{0.2})Sr_2YCu_2O_y$ (y = 7.8-8.1). Peaks due to SrRuO₃, CuO and unknown impurity phases are labeled by *.

They were almost single-phase 1212-type samples, though SrRuO₃ and other unknown impurities were formed in the y = 8.1 sample. The *c*-dimension tends to extend with the increase of the oxygen content, similarly to the case of x = 0.1. Magnetic susceptibility data of the x = 0.2 samples are shown in Fig. 12. The appearance of the ferromagnetism was affected by the oxygen content in a very complicated way. In the y = 7.9 sample, the ferromagnetism was, compared with the y = 7.8one, suppressed drastically with a low transition temperature of approximately 120 K and a small



Fig. 12. DC susceptibility data of the samples corresponding to Fig. 11.



Fig. 13. DC resistivity of the samples corresponding to Fig. 11.

ferromagnetic moment. When the oxygen content was increased to 8.0 and 8.1, the ferromagnetism was recovered again. The additional ferromagnetic-like transition at 27 K was observed in the y = 8.0 and 8.1 samples.

Diamagnetic moments were observed both in the ZFC and FC measurements for all samples and superconducting volume fraction at 5 K tends to increase with increasing the oxygen content. The superconducting transition temperature also tends to raise with the oxygen content from 43 K in y = 7.8 to 65 K in y = 8.1. As shown in Fig. 13, normal-state resistivity decrease drastically in the high-oxygen content samples and zero-resistivity was attained in x = 8.0 and 8.1. Nevertheless, the normal-state resistivity values of these two samples were at least one order of magnitude higher than those of normal cuprate superconductors.

The aforementioned experimental results can be summarized as follows:

- (1) There is a solid solution of $(Ru_{1-x}Cu_x)Sr_2$ -YCu₂O_y and its range terminates at $x \sim 0.1$ without formation of the stoichiometric phase of RuSr₂YCu₂O_y.
- (2) Oxygen content y in the $(Ru_{1-x}Cu_x)Sr_2$ -YCu₂O_y phase is also variable.
- (3) Superconductivity is largely affected by the oxygen content *y*. Superconducting transition

temperature tends to be raised with increasing the oxygen content of starting mixture.

- (4) Ferromagnetism tends to be suppressed by increasing the Cu content, *x*.
- (5) Influence of oxygen content on the ferromagnetism is not always simple. In the case of the x = 0.2 samples, ferromagnetic behavior changes in a complicated way as a function of the *y*-value.
- (6) High-pressure samples show high normal-state resistivities even when they have large diamagnetic susceptibilities at low temperatures.

Through the present experiment, we cannot confirm the coexistence of ferromagnetism and superconductivity for the Y-based system. On the contrary, the present results seem to cast doubt for the coexistence. The normal-state resistivity is always very high even when a sample shows a large diamagnetic susceptibility. The apparent coexistence of superconductivity and ferromagnetism may be explained by assuming a phase separation in a sample regarding the Ru/Cu ratio, i.e., superconductivity may be ascribed to Ru-poor grains with large x values while the ferromagnetism to Rurich grains with small x values which have semiconducting nature. However, two parameters of the Ru/Cu ratio and the oxygen content affect the superconductivity and ferromagnetism, and it makes the system quite complex. We need further studies for the final conclusion.

3.2. $RuSr_2LnCu_2O_8$ (Ln = Dy, Ho, Er) phase

In order to obtain $RuSr_2LnCu_2O_8$ (Ln = Dy, Ho, Er, Tm, Yb, Lu) phases, we first tested the stoichiometric compositions at 1200 °C and 6 GPa. Only for Ln = Dy, Ho and Er, the 1212-type phases were formed, while other systems were crystallized in simple perovskite structures. In the samples of Ln = Dy, Ho and Er, SrRuO₃ was included as an impurity phase. However, the impurity phase disappeared by starting from the Ru-poor compositions as well as in the Ln = Y system. Fig. 14 shows the powder X-ray diffraction patterns of the Ru_{0.9}Sr₂LnCu₂O_{7.8} (Ln = Dy,



Fig. 14. Powder X-ray diffraction patterns of the sample having nominal composition, $Ru_{0.9}Sr_2LnCu_2O_{7.8}$ (Ln = Dy, Ho, Er).



Fig. 15. DC susceptibility data of the samples corresponding to Fig. 14. Insert in (c) indicates DC resistivity of the Ln = Er sample.

Ho, Er) samples. Single-phase 1212 samples were obtained for the three systems.

DC susceptibility data are shown in Fig. 15 for the three single-phase samples. All samples exhibited ferromagnetic transitions near 170 K and only the Ln = Er sample showed diamagnetism below 43 K. However, in DC resistivity data of the Ln = Er sample (insert in Fig. 15(c)), zero-resistivity was not observed until 5 K though resistivity tended to decrease below 23 K. Moreover, resistivity value was quite high like the Ln = Y system. We cannot confirm the coexistence of ferromagnetism and superconductivity for the Ln = Er system as well as for the Ln = Y system.

4. Conclusion

We prepared the 1212-type ruthenate-cuprates $RuSr_2LnCu_2O_8$ (Ln = Y, Dy, Ho, Er) at 1200-1300 °C under 6 GPa. For the Ln = Y phase, highpurity sample was obtained with the Ru-poor starting composition, Ru_{0.9}Sr₂YCu₂O_{7.8}, treated at 1200 °C. According to DC susceptibility measurements, it showed the ferromagnetism near 150 K but with minimal diamagnetic susceptibility. On the other hand, the sample prepared at 1300 °C with a higher oxygen content, Ru_{0.9}Sr₂YCu₂O_{7.9}, underwent ferromagnetic transition near 150 K followed by diamagnetic transition at 37 K. Both samples did not show zero-resistivity and had quite high resistivity values compared with normal cuprate superconductors. After O₂-HIP posttreatment, these samples showed zero-resistivity but decomposition of the 1212 phases occurred.

The EPMA analysis suggested existence of Ru-poor grains in the samples and formation of solid solution of $(Ru_{1-x}Cu_x)Sr_2YCu_2O_8$. Indeed, we could obtain the single-phase sample of $(Ru_{1-x}Cu_x)Sr_2YCu_2O_y$ in the range of x = 0.1-0.3 at 1300 °C. Superconductivity and ferromagnetism were largely affected by the Ru/Cu ratio and the oxygen content *y*. Superconducting transition temperature tends to be raised with increasing the oxygen content while ferromagnetism tends to be suppressed by increasing the Cu content. In spite of testing many samples, we could not confirm the coexistence of ferromagnetism and superconduct-

tivity for the Y-based system. On the contrary, the present results seem to cast doubt for the coexistence because the normal-state resistivity is always very high even when a sample shows a large diamagnetic susceptibility. The apparent coexistence of superconductivity and ferromagnetism may be explained by assuming a phase separation in a sample regarding the Ru/Cu ratio for the solid solution of $(Ru_{1-x}Cu_x)Sr_2YCu_2O_y$.

For Ln = Dy, Ho and Er systems, single-phase 1212 samples were obtained with the Ru-poor starting composition as well as in the Ln = Y system. According to DC susceptibility measurements, every sample exhibited a ferromagnetic transition near 170 K and only Ln = Er sample showed diamagnetism below 43 K. However, it had high resistivity and zero-resistivity was not attained.

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References

- J.L. Tallon, C. Bernhard, M.E. Bowden, P.W. Gilberd, T.M. Stoto, D.J. Pringle, IEEE Trans. Appl. Supercond. 9 (1999) 1696.
- [2] C. Bernhard, J.L. Tallon, Ch. Niedermayer, Th. Blasius, A. Golnik, E. Brucher, R.K. Kremer, D.R. Noakes, C.E. Stronach, E.J. Ansaldo, J. Phys. Rev. B 59 (1999) 14099.
- [3] D.J. Pringle, J.L. Tallon, B.G. Walker, H.J. Trodahl, Phys. Rev. B 59 (1999) 11679.
- [4] A.C. McLaughlin, W. Zhou, J.P. Attfield, A.N. Fitch, J.L. Tallon, Phys. Rev. B 60 (1999) 7512.
- [5] W.E. Pickett, R. Weht, A.B. Shick, Phys. Rev. Lett. 83 (1999) 3713.
- [6] A.C. McLaughlin, J.P. Attfield, Phys. Rev. B 60 (1999) 14605.
- [7] O. Chmaissen, J.D. Jorgensen, H. Shaked, P. Dollar, J.L. Tallon, Phys. Rev. B 61 (2000) 6401.

- [8] J.L. Tallon, J.W. Loram, G.V.M. Williams, C. Bernhard, Phys. Rev. B 61 (2000) 6471.
- [9] C.W. Chu, Y.Y. Xue, R.L. Meng, J. Cmaidalka, L.M. Dezaneti, Y.S. Wang, B. Lorenz, A.K. Heilman, cond-mat/ 9910056, unpublished.
- [10] C. Bernhard, J.L. Tallon, E. Brucher, R.K. Kremer, Phys. Rev. B 61 (2000) 14960.
- [11] J.W. Lynn, B. Keimer, C. Ulrich, C. Bernhard, J.L. Tallon, Phys. Rev. B 61 (2000) 14964.
- [12] A. Fainstein, P. Etchegoin, H.J. Trodahl, J.L. Tallon, Phys. Rev. B 61 (2000) 15468.
- [13] A.P. Litvinchuk, M.N. Iliev, Y.-Y. Xue, R.L. Meng, C.W. Chu, Phys. Rev. B 62 (2000) 9709.
- [14] J.-X. Zhu, C.S. Ting, C.W. Chu, Phys. Rev. B 62 (2000) 11369.
- [15] K. Nakamura, K.T. Park, A.J. Freeman, J.D. Jorgensen, Phys. Rev. B 63 (2000) 024507.
- [16] J.D. Jorgensen, O. Chmaissem, H. Shaked, S. Short, P.W. Klamut, B. Dabrowski, J.L. Tallon, Phys. Rev. B 63 (2000) 054440.
- [17] P.W. Klamut, B. Dabrowski, M. Maxwell, J. Mais, O. Chmaissem, R. Kruk, R. Kmiec, C.W. Kimball, Physica C 341–348 (2000) 455.
- [18] X.H. Chen, Z. Sun, K.Q. Wang, S.Y. Li, Y.M. Xiong, M. Yu, L.Z. Cao, Phys. Rev. B 63 (2001) 064506.
- [19] K. Kumagai, S. Takada, Y. Furukawa, Phys. Rev. B 63 (2001) 180509.
- [20] A.V. Boris, P. Mandal, C. Bernhard, N.N. Kovaleva, K. Pucher, J. Hemberger, A. Loidl, Phys. Rev. B 63 (2001) 184505.
- [21] R.S. Liu, L.-Y. Jang, H.-H. Hung, J.L. Tallon, Phys. Rev. B 63 (2001) 212507.
- [22] P.W. Klamut, B. Dabrowski, S. Kolesnik, M. Maxwell, J. Mais, Phys. Rev. B 63 (2001) 224512.

- [23] Y. Tokunaga, H. Kotegawa, K. Ishida, Y. Kitaoka, H. Takagiwa, J. Akimitsu, J. Phys. Rev. Lett. 86 (2001) 5767.
- [24] P.W. Klamut, B. Dabrowski, J. Mais, M. Maxwell, Physica C 350 (2001) 24.
- [25] P.W. Klamut, B. Dabrowski, S.M. Mini, M. Maxwell, S. Kolesnik, J. Mais, A. Shengelaya, R. Khasanov, I. Savic, H. Keller, T. Graber, J. Gebhardt, P.J. Viccaro, Y. Xiao, Physica C 364–365 (2001) 313.
- [26] A.C. Mclaughlin, V. Janowitz, J.A. McAllister, J.P. Attfield, J. Mater. Chem. 11 (2001) 173.
- [27] P.W. Klamut, B. Dabrowski, S.M. Mini, S. Kolesnik, M. Maxwell, A. Shengelaya, R. Khasanov, H. Keller, I. Savic, C. Sulkowski, M. Matusiak, A. Wisniewski, R. Puzniak, I. Fita, J. Appl. Phys. 91 (2002) 7134.
- [28] R. Ruiz-Bustos, J.M. Gallardo-Amores, E. Moran, V. Garcia-Baonza, M.A. Alario-Franco, High Press. Res. 22 (2002) 573.
- [29] R. Kruk, R. Kmiec, P.W. Klamut, B. Dabrowski, D.E. Brown, M. Maxwell, C.W. Kimball, Physica C 370 (2002) 71.
- [30] R. Ruiz-Bustos, J.M. Gallardo-Amores, R. Saez-Puche, E. Moran, M.A. Alario-Franco, Physica C 382 (2002) 395.
- [31] L. Bauernfeind, W. Widder, H.F. Braun, Physica C 254 (1995) 151.
- [32] H. Takagiwa, J. Akimitsu, H. Kawano-Furukawa, H. Yoshizawa, Phys. Soc. Jpn. 70 (2001) 333.
- [33] H. Takagiwa, private communication, 2001.
- [34] A. Callaghan, C.W. Moeller, R. Ward, Inorg. Chem. 5 (1966) 1572.
- [35] For example L. Bauernfeind, W. Widder, H.F. Braun, J. Low Temp. Phys. 105 (1996) 1605.
- [36] P.D. Battle, W.J. Macklin, J. Solid State Chem. 52 (1984) 138.