Pertanika J. Sci. & Technol. 13(1): 127 - 138 (2005)
ISSN: 0128-7680

Superconductivity in Layerd Cuprate $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$

R. Abd-Shukor*, C. A. Kek & W. K. Yeoh
School of Applied Physics
Universiti Kebangsaan Malaysia
43600 Bangi, Selangor, Malaysia

Received: 25 May 2004

ABSTRAK

Satu siri bahan kuprat berrlapis $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ (Ru1212) dengan $0 \leq x \leq 1$ telah disintesis melalui kaedah tindakbalas keadaan pepejal. Analisis pembelauan sinar-X sampel bentuk serbuk menunjukkan bahawa pengaliran oksigen adalah penting bagi sampel dengan fasa Ru1212 dan kesuperkonduktoran sistem ini. Corak pembelauan bagi sampel dengan komposisi nominal $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ boleh diindeks sebagai struktur tetragonal dengan kumpulan ruang P4/mmm. Bahan kurang dop menunjukkan suhu genting (T_c) tertinggi dengan $T_{c\ mula}$ 65 K dan $T_{c\ sifar}$ 55 K. Kajian ini menunjukkan bahawa pendopan dengan Nb menurunkan kekonduksian keadaan biasa dan menekan kesuperkonduksian sistem.

ABSTRACT

A series of layered cuprate $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ (Ru1212) for $0 \leq x \leq 1$ has been synthesized by the solid state reaction method. Powder X-ray diffraction analysis indicates that oxygen flow is important in the formation of the Ru1212 phase and superconductivity in the system. Samples with nominal composition $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ can be indexed as a tetragonal structure with space group P4/mmm. The undoped compound exhibits the highest superconducting transition with $T_{c\ onset}$ of 65 K and $T_{c\ zero}$ of 55 K. Our results also show that doping with Nb decreases the normal state conductivity and suppresses superconductivity in the system.

Keywords: Electrical resistance, Ru-based superconductor, transition temperature
PACS No.: 74.25.Fy, 74.62.Bf, 74.72.Jt

INTRODUCTION

The remarkable coexistence of ferromagnetism and superconductivity in $RuSr_2GdCu_2O_8$ (Ru1212) has been of enormous interest in the past few years (Wang *et al.* 2003; Tallon *et al.* 2000; Felner *et al.* 1999; Bernhard et al. 1999; Matveev *et al.* 2004). Ferromagnetism in this material was considered to be due to the RuO_2 sublattice with $4d^3$ high spin state and the superconductivity originates from CuO_2 layers, similar to that observed in the superconducting layered cuprate $RuSr_2(Gd,Ce)_2Cu_2O_z$ (Ru1222). These materials are the first cuprate superconductors with magnetic ordering transition $T_m > T_c$. Usually these with two order parameters mutually destroy each other but this nonuniform

* Corresponding author
Email: ras@pkrisc.cc.ukm.my

ferromagnet might be ordered in the form of a spiral structure or a domain-like structure such as the Chevrel compound $HoMo_6S_8$ (Chu *et al.* 2000). Neutron scattering studies have shown that the Ru-spins order antiferromagnetically with Ru moments forming the G-type AFM structure (Lynn *et al.* 2000). An interesting comparison between the pairing state of the Cu oxide and Ru oxide based superconductors has also been reported recently (Sugahara *et al.* 2004).

The nonsuperconductive $MBa_2LaCu_2O_8$, M=Nb (Vybornov *et al.* 1995) has been successfully synthesized from the parent material of $YBa_2Cu_3O_{7-\delta}$ by replacing the Cu-O chain with a single octahedral plane (MO_2) between the apices pyramidal CuO_2 planes and Y with La respectively. Results from recent band structure calculations for $LaBa_2NbCu_2O_8$ and $BaLa_2Cu_2TiO_8$, predict that a pair of nearly degenerate and half-filled s -antibonding subbands in these materials might become superconductor if they could be properly doped or prepared under appropriate conditions (Mattheis 1992). The ruthenium based layered cuprate was first reported by Bauerfeind *et al.* (1995) with T_c = 42 K and T_m = 133 K for Ru1212, and T_c = 45 K and T_m = 180 K for Ru1222.

In this paper we report the effect of niobium substitution in the RuO_2 sublattice to elucidate the nature of superconductivity in the Ru1212 material. Niobium was chosen due to the d^0 configuration (fully ionized transition-metal) and is believed to lead to change in conducting property. This assertion becomes evident when Z. Sun *et al.* (2001) successfully demonstrated superconductivity in $(Ru_{1-x}Ta_x)Sr_2GdCu_2O_8$.

MATERIALS AND METHODS

Samples with nominal compositions $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ for x 0 x 1 were prepared by the solid state reaction method from starting oxides of RuO_2 (99.999 %), Nb_2O_5 (99.99 %), $SrCO_3$ (99.9+ %), Gd_2O_3 (99.999 %) and CuO (99.999 %). The mixed powder was thoroughly ground and calcined in air at 980 °C for 48 hours with intermediate grindings. A calcination step is performed to decompose the carbonates. Then, the resulting powders were ground and pressed into pellets. The first annealing step at 1010 °C was performed in flowing nitrogen for 10 hours. Then, the samples were reground and pelletised. The pellets were then annealed at 1050 °C for 24 hours in flowing oxygen. Finally, the samples were slowly cooled at the rate of 1 °C/min to 300 °C in flowing oxygen to avoid freezing of disorder. Both prereaction and sintering were performed in alumina crucibles.

The powder X-ray diffraction method using a Siemens D 5000 diffractometer with CuK_α source has been used to identify the resultant phase. The volume fractions are estimated by comparing the highest intensity peak for each phase. The d.c. electrical resistance-temperature measurement was carried out by the four point probe technique with silver paste contacts in a CTI Closed Cycle Refrigerator down to about 8 K.

RESULTS AND DISCUSSION

In order to properly evaluate the purity of 1212 phase of $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ system, powder XRD measurements were performed after each heat treatment. The powder X-ray diffraction patterns after sintering in air of $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ samples with $x = 0.00$, 0.05, 0.08, 0.10 and $x = 0.15$, 0.20, 0.45, 0.50 are shown in *Fig. 1(a)* and *1(b)* respectively. The results show that the 1212 phase is the dominant phase. These results reflect that the 1212 phase can be stabilized with partial substitution of Nb ions into the Ru site. However, $Sr(Ru,Nb)O_3$ marked with (#) phase (Lorenz *et al.* 2001) is found as secondary phase at about $2\theta = 31.8^o$ together with small amounts of $(Ru,Nb)Sr_2GdO_6$ (+) and CuO (*) in the doped samples. The 1212 phase gradually decreases while the secondary phase of $Sr(Ru,Nb)O_3$ is increased as the Nb content is increased. This finding suggests that the M1212, M = Ru and Nb are very sensitive to the reaction temperature and the reaction temperature between 960°C - 980 °C might be optimum for the Ru-system to form a pure 1212 phase but it is too low for the formation of Nb1212.

In *Fig. 2*, the powder X-ray diffraction patterns after the heat treatment in reducing atmosphere clearly implies the absence of any phase with 1212 structure. However, the main phase is likely to appear as unreacted CuO and a cubic perovskite of the form $(Ru,Nb)Sr_2GdO_6$. This step is important to

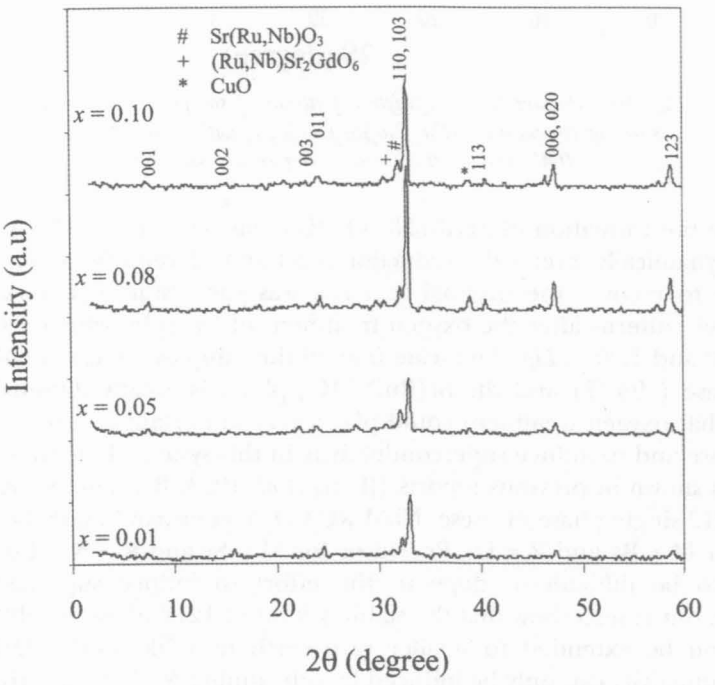

Fig. 1(a): Powder X-ray diffraction patterns of samples with nominal starting composition $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ with x =0.01, 0.05, 0.08 and 0.10 after sintering in air for 48 h

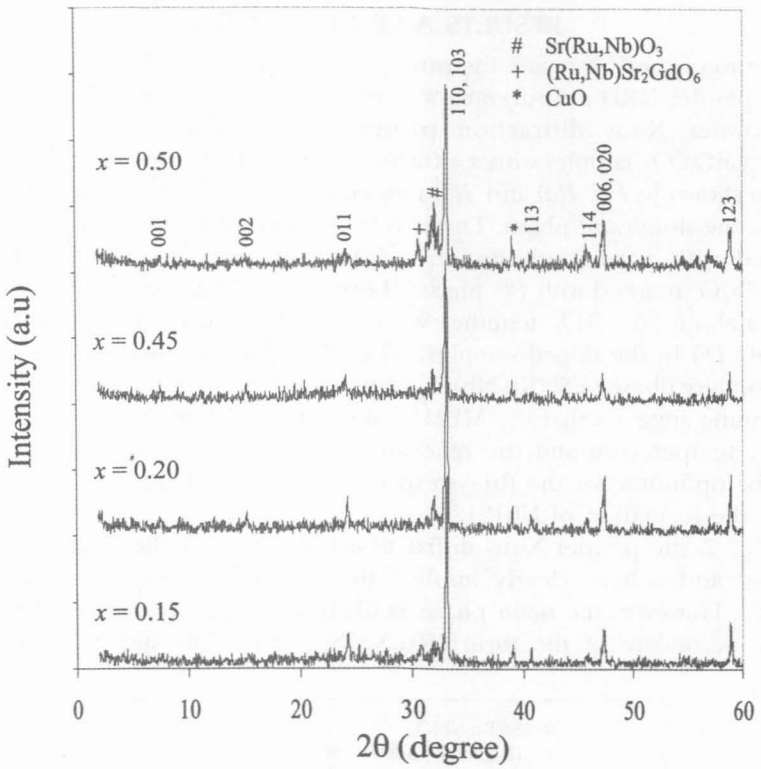

Fig. 1(b): Powder X-ray diffraction patterns of samples with nominal starting composition $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ *with* x *=0.15, 0.20, 0.45 and 0.50 after sintering in air for 48 h*

minimize the formation of $Sr(Ru,Nb)O_3$ (Chmaissem *et al.* 2000). Attempts to thermodynamically reverse this reduction reaction with reintroduction of oxygen in order to recover the original material was successful. The powder X-ray diffraction patterns after the oxygen treatment of samples with x = 0.08, 0.20, 0.40, 0.60 and 1.00 in *Fig. 3* indicate that all the samples are essentially a single 1212 phase (>98 %) and the $Sr(Ru,Nb)O_3$ phase is greatly diminished. This implies that oxygen treatment could play a very important role to stabilize the 1212 phase and to induce superconductivity in this system (Klamut *et al.* 2001).

It was shown in previous reports (Jhans *et al.* 1993; Bennahmias *et al.* 1992) that a 1212 single phase of these $NbM_2RCu_2O_8$ systems could only be stabilized for either M = Ba and R = La, Pr, Nd or for M = Sr and R = Nd, Eu and have proven to be difficult to dope in the effort to induce superconductivity. However, our results show that the stability limit of 1212 phase in $NbSr_2RCu_2O_8$ system can be extended to smaller rare earth ions like Gd^{3+} (0.94 Å) and superconductivity can only be induced by substituting Ru ions into the Nb ions sites.

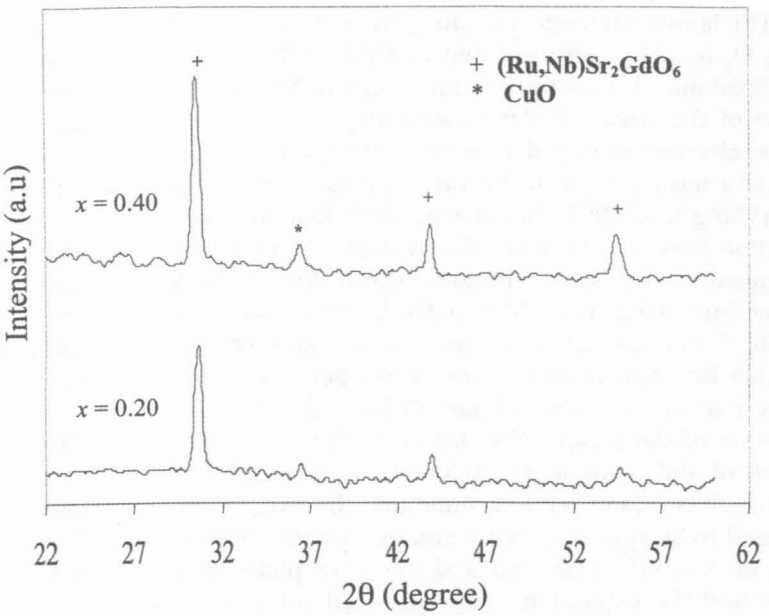

Fig. 2: Powder X-ray diffraction patterns of samples with nominal starting composition $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ after heat treatment in reduction atmosphere which clearly imply the absence of the 1212 phase

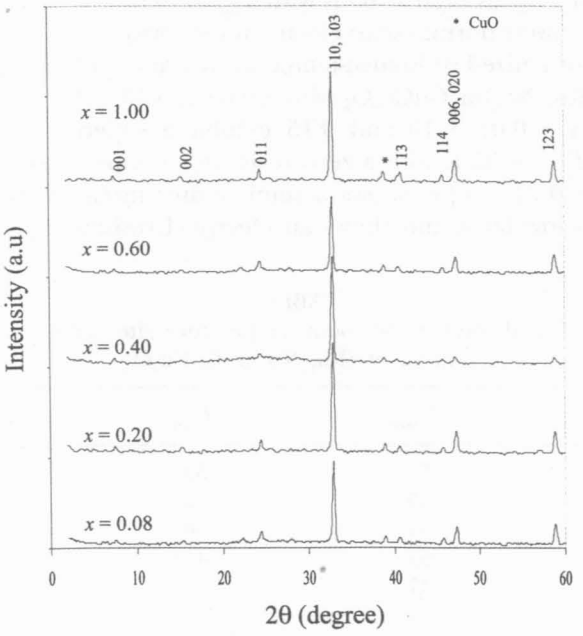

Fig. 3: Powder X-ray diffraction patterns of samples with nominal starting composition $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ with x =0.08, 0.20, 0.40, 0.60 and 1.00 after annealing in flowing oxygen for 24 h

The lattice parameters of $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ system after annealing in flowing O_2 for 24 hours are listed in Table 2. The lattice parameters *a*, *c* and unit cell volume, *V* increase with increasing of Nb content. This is shown by the increase of the *a*-axis with the increasing of Nb content. It suggests that an effective electron is doped into the antibonding part of CuO orbital which results in a tensile stress in the CuO and thereby lengthens the in-plane CuO bonds (Wang *et al.* 1997; Awana *et al.* 1996; Klamut *et al.* 2001). It is interesting to mention here that Ru can exist in single valence state either in 4+ or in 5+ or in mixed valence state. The ionic size of Ru^{5+} (0.57 Å) is smaller than that of either Ru^{4+} (0.62 Å) or Nb^{5+} (0.64 Å). Since the lattice parameter *c* of the $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ system is seen to increase with *x*, crystallographically it seems that Ru exists more towards its 5+ valence state in this system. Thus, the expansion of the unit cell volume of this system is believed to be due to the substitution of the greater Nb^{5+} ions into the smaller Ru^{5+} ions. However, the presence of Ru^{4+} cannot be excluded (Tang *et al.* 1997; Tang *et al.* 1996). Therefore, it is reasonable to assume that the oxygen content of the cuprate is considered to be approximately 8 and the structure of Ru-1212 would be similar to that of Nb-1212. Based on a single 1212 phase that is observed in XRD patterns and the expansion of the unit cell volume in $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ system, we conclude that the Nb ions are readily incorporated into the structure.

The electrical resistivity *vs.* temperature measurement for the $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ sample with $x = 0.00$ is shown in *Fig. 4*. The undoped sample exhibits metallic normal state until 100 K where a semiconducting upturn occurred and a $T_{c\text{-}onset}$ as high as 65 K with $T_{c\text{-}zero}$ of 55 K is observed. This sample also shows the lowest normal state electrical resistivity (Table 1). *Fig. 5* and *Fig. 6* display the normalized resistance-temperature curve for samples with nominal composition $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ with $x = 0.01$, 0.10, 0.15, 0.20 and 1.00. The samples with $x = 0.01$, 0.10 and 0.15 exhibit a superconducting transition temperature, $T_{c\text{-}onset} \sim 55$ K with a zero resistance temperature, $T_{c\text{-}zero} \sim 40$ K. In *Fig. 6*, the $x = 0.20$ sample shows a semiconducting/insulating transition in normal state below 60 K and shows an electrical resistance anomaly at 50 K.

TABLE 1
T_c and resistivity at room temperature after sintering in air of $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$

x	$T_{c\text{-}onset}$	$T_{c\text{-}zero}$	ρ (mΩ-cm)
0.00	65	55	10.0
0.01	56	41	12.0
0.10	54	40	12.7
0.15	55	41	12.8
0.20	47	-	13.0
0.40	-	-	14.8
0.60	-	-	22.8
1.00	-	-	278

TABLE 2
Lattice parameters and unit cell volume of $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ after annealing in flowing oxygen for 24 h

x	a (Å)	c (Å)	V (Å^3)
0.00	3.841 (2)	11.532 (15)	170.1
0.08	3.845 (2)	11.554 (13)	170.8
0.20	3.849 (3)	11.558 (15)	171.2
0.40	3.854 (2)	11.566 (12)	171.8
0.60	3.856 (3)	11.591 (17)	172.3
1.00	3.866 (3)	11.633 (18)	173.9

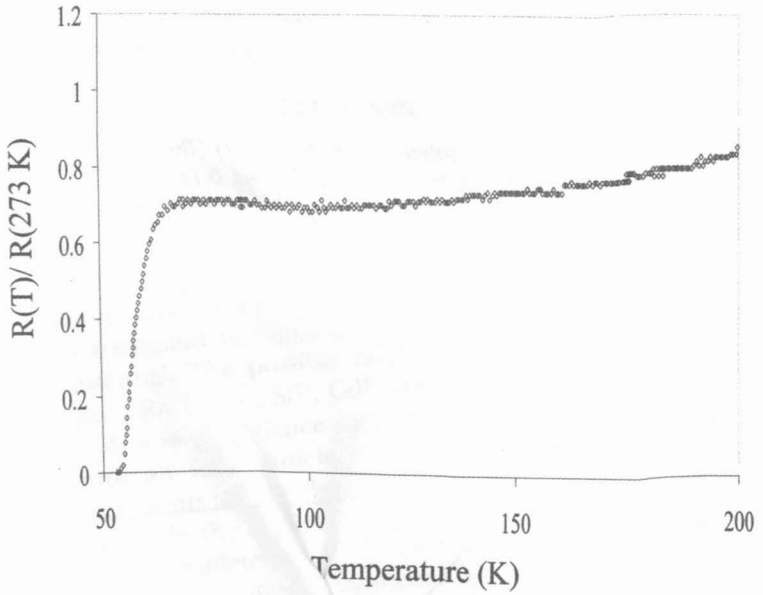

Fig. 4: Electrical resistance vs temperature of $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$ for x = 0.00 which exhibits the highest superconducting transition at $T_{c\text{-onset}}$ = 65 K with $T_{c\text{-zero}}$ = 55 K

This means that the superconducting property was completely destroyed at about 20 % of Nb substitution. The sample with x = 1.00 exhibits an insulator-like behavior in good agreement with the previous reports (Vybornov *et al.* 1995 and Greaves *et al.* 1989) without any superconducting transition.

The presence of Nb ions dramatically changes the normal state behavior of the samples from metallic to semimetallic. This is followed by a narrow gap semiconducting-like behavior with increasing doping level. The sample exhibits a large gap semiconducting-like behavior when the Ru ions are fully replaced by Nb ions. The resistivity as a function of x (Nb content) at room temperature corresponds well with their normal state behaviors shown in *Fig. 7*. The room

oxygen is necessary to stabilize the 1212 phase and to induce superconductivity in $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$. Annealing in flowing nitrogen does not stabilize the 1212 phase. The undoped compound exhibits the best superconducting behaviour with onset superconducting transition at 65 K and zero resistance temperature at 55 K. Superconductivity is suppressed in the Nb-doped samples (x = 0.01, 0.10 and 0.15) with $T_{c\text{-}onset} \sim 55$ K and $T_{c\text{-}zero} \sim 40$ K. Superconductivity was completely destroyed when 20 % of Nb was doped in $(Ru_{1-x}Nb_x)Sr_2GdCu_2O_8$.

Oxygen deficiency in $RuSr_2GdCu_2O_{8\pm\delta}$ with δ = 0.2-0.3 so that it exhibits superconductivity is not probable. On the other hand, Ru may be in mixed valence state $Ru^{4+/5+}$ and $(Ru,Nb)Sr_2GdCu_2O_8$ is supposed to be fully oxygenated after undergoing long treatment in O_2 flowing (24 hours or more). In this case, the average valence of Ru is suggested to be between 4.4+ and 4.6+.

ACKNOWLEDGEMENTS

This research has been supported by IRPA project no. 09-02-02-0072EA199 from the Ministry of Science, Technology and Innovation, Malaysia.

REFERENCES

AWANA, V.P.S., L. MENON and S.K. MALIK. 1996. Effect of substituting Ce at the Ca site on the high-temperature superconductor $Bi_2Sr_2CaCu_2O_{8+d}$. *Phys. Rev. B* **53:** 2245-2248.

BAUERNFEIND, L., W. WIDDER and H.F. BRAUN. 1995. Ruthenium-based layered cuprates $RuSr_2LnCu_2O_8$ and $RuSr_2(Ln_{1+x}Ce_{1-x})Cu_2O_{10}$ (Ln = Sm, Eu and Gd). *Physica C* **254**: 151-158.

BENNAHMIAS, M., J.C. O'BRIEN, H.B. RADOUSKY, J.T. GOODWIN, P. KLAVINS, J.M. LINK, C.A. SMITH and R.N. SHELTON. 1992. Magnetic, structural, and Raman characterization of $RBa_2Cu_2NbO_8$ (R=Pr, La, or Nd). *Phys. Rev. B* **46:** 11986-11992.

BERNHARD, C., J.L. TALLON, CH. NIEDERMAYER, TH. BLASIUS, A. GOLNIK, E. BRÜCHER, R.K. KREMER, D.R. NOAKES, C.E. STRONACH and E.J. ANSALDO. 1999. Coexistence of ferromagnetism and superconductivity in the hybrid ruthenate-cuprate compound $RuSr_2GdCu_2O_8$ studied by the muon spin rotation and dc magnetization. *Phys. Rev. B* **59:** 14099-14107.

BUTERA, A., A. FAINSTEIN, E. WINKLER and J.L. TALLON. 2001. Ferromagnetic correlarions and mixed Ru valence in the magnetic superconductor $RuSr_2(Eu,Gd)Cu_2O_8$. *Phys. Rev. B* **63:** 054442(1-4).

CHMAISSEM, O., J.S. JORGENSEN, H. SHAKED, P. DOLLAR and J.L. TALLON. 2000. Crystal and magnetic structure of ferromagnetic superconducting $RuSr_2GdCu_2O_8$, *Phys. Rev. B* **61:** 6401-6407.

CHU, C.W., Y.Y. XUE, S. TSUI, J. CMAIDALKA, A.K. HEILMAN, B. LORENZ and R.L. MENG. 2000. A possible crypto-superconducting structure in a superconducting ferromagnet. *Physica C* **335:** 231-238.

FELNER, I., U. ASAF, S. REICH and Y. TSABBA. 1999. Magnetic properties of $RSr_2RuCu_2O_{8+d}$ (R=Eu and Gd). *Physica C* **311:** 163-171.

GREAVES, C. and P.R. SLATER. 1989. Nb and Ta substitutions in $YBa_2Cu_3O_{7-x}$ and related phases: structural characterization of $La_{1.1}Ba_{1.9}Cu_{2.1}M_{0.9}O_8$ (M= Nb, Ta). *Physica C* **161:** 245-251.

JHANS, H., S.K. MALIK and R. VIJAYARAGHAVAN. 1993. Synthesis and magnetic properties of the $R_{1+x}Sr_{2-x}Nb_{1-x}O_{8-y}$. *Physica C* **215:** 181-190.

KLAMUT, P.W., B. DABROWSKI, J. MAIS and M. MAXWELL. 2001. Effect of Ce doping on the superconducting and magnetic properties of $RuSr_2GdCu_2O_8$. *Physica C* **350:** 24-28.

KLAMUT, P.W., B. DABROWSKI, S.M. MINI, M. MAXWELL, S. KOLESNIK, J. MAIS, A. SHENGELAYA and R. KHASANOV, I. SAVIC, H. KELLER, T. GRABER, J. GEBHARDT, P.J. VICCARO and Y. XIAO. 2001. Magnetic properties of $RuSr_2RECu_2O_8$ (RE=Gd, Eu) and $Ru_{1-x}Sr_2GdCu_{2+x}O_{8-y}$ superconductors. *Physica C* **364-365:** 313-319.

LIU, R.S., L.Y. JANG, H.H. HUNG and J.L. TALLON. 2001. Determination of Ru valence X-Ray absoprtion near-edge structure in $RuSr_2(Gd,Ce)_2Cu_2O_8$-Type superconductor. *Phys. Rev. B* **63:** 212507(1-5).

LORENZ, B., R.L. MENG, J. CMAIDALKA, Y.S. WANG, J. LENZI, Y.Y. XUE and C.W. CHU. 2001. Synthesis, characterization and physical properties of the superconducting ferromagnet $RuSr_2GdCu_2O_8$. *Physica C* **363:** 251-259.

LYNN, J.W., B. KEIMER, C. ULRICH, C. BERNHARD and J.L. TALLON. 2000. Evidence for a Bulk Meissner State in a Ferromagnetic Superconductor $RuSr_2GdCu_2O_8$ from dc Magnetization. *Phys. Rev. B* **61:** R14960-R14963.

MATTHEISS, L.F. 1992. Electronic structure of $LaBa_2Cu_2NbO_8$ and related candidates for High-T_c superconductivity. *Phys. Rev. B* **45:** 2442-2446.

MATVEEV, A.T., E. SADER, V. DUPPEL, A. KULAKOV, A. MALJUK, C.T. LIN and H.U. HABERMEIER. 2004. Decomposition of $RuSr_2GdCu_2O_8$ phase under high-temperature treatment. *Physica C* **403:** 231-239.

SUGAHARA, M. and Jr. N.N. BOGOLUBOV. 2004. Unified model of superconductivity of singlet-pair Cu oxide superconductor and triplet-pair Ru oxide superconductor, *International J. of Mod. Phys. B* **18:** 71-86.

SUN, Z., S.Y. LI, Y.M. XIONG and X.H. CHEN. 2001. Preparation, Structure, and Superconductivity of Ru1222 and Ta-Doped Ru1212. *Physica C* **349:** 289-294.

TALLON, J.L., J.W. LORAM, G.V.M. WILLIAMS and C. BERNHARD. 2000. Heat capacity and transport studies of the ferromagnetic superconductor $RuSr_2GdCu_2O_8$. *Phys. Rev. B* **61:** R6471-R6474.

TANG, K.B., Y.T. QIAN, L. YANG, Y.D. ZHAO and Y.H. ZHANG. 1997. Crystal structure of a new series of 1212 type cuprate $RuSr_2LnCu_2O_z$. *Physica C* **282 – 287:** 947-948.

TANG, K.B., Y.T. QIAN, Y.D. ZHAO, L. YANG, Z.Y. CHEN and Y.H. ZHANG. 1996. Synthesis and characterization of a new layered superconducting cuprate: $RuSr_2(Gd,Ce)_2Cu_2O_{10}$. *Physica C* **259:** 168-172.

VYBORNOV, M., W. PERTHOLD, H. MICHOR, T. HOLUBAR, G. HILSCHER, P. ROGL, P. FISCHER and M. DIVIS. 1995. Synthesis and characterization of compounds $Sr_2RMCu_2O_{8-d}$ (*R*=Pr, Nd, Sm, Eu, Gd; *M*=Nb, Ta). *Phys. Rev. B* **52:** 1389-1404.

WANG, C., C. DONG, G. CHE, Z.Y. QIAO, H. CHEN and Z.H. ZHAO. 1997. Relationship between the lattice parameter and superconductivity in the 2-1-4 Series N-Type Cuprates. *Phys. Rev. B* **55:** 3935-3942.

WANG, D.Z., H.I. HA, J.I. OH, J. MOSER, J.G. WEN, M.J. NAUGHTON and Z.F. REN. 2003. Synthesis and Properties of Superconductor $RuSr_2GdCu_2O_8$. *Physica C* **384:** 137-142.