Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 2, 425–429

HEAT CAPACITY OF GdBaSr($Cu_{3-x}M_x$)$O_{7-\delta}$ SUPERCONDUCTOR (M=Zn AND Ni)

T. V. Chong[1], *S. Kambe*[1*], *H. Kawaji*[2], *T. Atake*[2] *and O. Ishii*[1]

[1]Yamagata University, Graduate School of Science and Engineering, Human Sensing Program, 4-3-16 Johnan, Yonezawa City Yamagata, 992-8510, Japan
[2]Tokyo Institute of Technology, Materials and Structures Laboratory, 4259 Nagatsuta-cho, Midori-ku, Yokohama, 226-8503, Japan

In this study, GdBaSr($Cu_{3-x}M_x$)$O_{7-\delta}$ bulk samples (M=Zn and Ni; $0\leq x\leq 0.1$) were prepared via solid-state reaction. Specific heat measurement (measured with thermal relaxation technique using PPMS) shows an obvious specific heat jump around the T_c for $GdBaSrCu_3O_{7-\delta}$ sample as observed in most of the high temperature superconductors. It shifts towards lower temperature with increasing of both Zn and Ni doping contents, whose tendency is similar to the decreasing of T_c. Debye temperature, Θ_D (derived from specific heat measurements) calculated at around 10 K is found to be directly proportional to the T_c.

Keywords: *Debye temperature, $GdBaSrCu_3O_{7-\delta}$, Ni doping, specific heat, Zn doping*

Introduction

It is generally known that CuO_2 planes of layered cuprate superconductors play a major role in the variation of critical temperature, T_c. Superconductivity is believed to occur in the Cu(2)–O_2 sheets through hole charge carriers, and the oxygen content of Cu(1)–O chains governs the hole carries concentration in the Cu(2)–O_2 sheets. Previous studies on Zn doped $YBa_2Cu_3O_7$ superconductors showed Zn atoms mainly take the Cu(2) sites in the CuO_2 planes and such substitution may be useful in understanding the mechanism of superconductivity in these materials [1, 2]. Zn^{2+} as a non-magnetic ion, disrupts the local antiferromagnetic correlation of Cu(2) spin and thereby induces a localized paramagnetic moment shared by four neighbouring Cu(2) sites [3, 4]. Since the ionic size and orbital structure of 3*d* elements are closed to those of Cu, 3*d* elements will occupy the Cu sites if they are substituted into Cu-based high temperature superconductors.

Besides, the lattice vibration is expected to influence strongly the electronic properties of high temperature superconductors (HTSC) especially at low temperature below the T_c. Recently, various experimental results point towards the important role of phonons in the mechanism of cuprate high temperature superconductors ([5–7] and references therein). Behaviors of the specific heat measured at low temperature may probe into the point of the effect of phonons. Debye temperature derived from specific heat measurements may provide essential information about the role of phonon and its interaction with T_c as well and this may be very useful for the determination of the possible mechanism of HTSC materials.

In this study, GdBaSr($Cu_{3-x}M_x$)$O_{7-\delta}$ bulk samples (M=Zn and Ni) where $0\leq x\leq 0.1$ were prepared via solid-state reaction. The tetragonal structure of $GdBaSrCu_3O_{7-\delta}$ sample perhaps easier to be investigated compare with other 123-system HTSC materials whose is in orthorhombic structure. Moreover, such doping should have significant effects on the electronic properties of these *d*-wave superconductors because of the contrast in magnetic properties of these elements. All samples were prepared under the same condition and hence, any significant variation of the result is assumed to be irrelevant to the samples' preparation. Specific heat of all samples were measured with thermal relaxation technique using PPMS.

Specific heat measurement from around 0 to 150 K shows an obvious specific heat jump around critical temperature for $GdBaSrCu_3O_{7-\delta}$ sample as observed in most of the high temperature superconductors. This specific heat jump seems like shifted to lower temperature upon increasing of both Zn and Ni doping contents, which is parallel to the decreasing of T_c. From the low temperature properties of specific heat, the changes in Debye temperature among these samples will be investigated and discussed in this communication. Besides, comparison between non-magnetic disturbances (Zn-doped samples) and magnetic disturbances (Ni-doped samples) on the antiferromagnetic CuO_2 plane were also studied.

* Author for correspondence: kambe@yz.yamagata-u.ac.jp

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Experimental

GdBaSr($Cu_{3-x}M_x$)$O_{7-\delta}$ (M=Zn and Ni; x=0, 0.01, 0.07 and 0.1) polycrystalline samples were prepared by mixing stoichiometric amounts of high purity (≥99.99%) Gd_2O_3, $BaCO_3$, $SrCO_3$, CuO, ZnO and NiO powders. The mixed powders were calcined in air at around 1223 K for 48 h with several intermittent grindings and natural cooled in furnace. The powders were then pressed into pellets. The pellets were sintered at 1223 K for another 24 h and natural cooled in furnace. The samples were then annealed in flowing of O_2 gas at 1223 K for more than 10 h to increase the oxygen content. After that, the samples were cooled at 353 K h^{-1} until 873 K and then natural cooled in furnace to room temperature.

The phases of these samples were examined by X-ray powder diffraction with CuK_α radiation using a RINT2000 Wilder-angle goniometer. From the lattice spacing (d) and relative identified miller index (h, k and l) of all peaks observed from XRD pattern, lattice constants (a, b and c) were calculated based on the formula below by manipulated using MathCAD software.

$$\frac{1}{d^2}=\left(\frac{h}{a}\right)^2+\left(\frac{k}{b}\right)^2+\left(\frac{l}{c}\right)^2$$

Scanning electron microscope (SEM) micrographs were recorded using a JSM-6300F scanning electron microscope to determine the variation of morphology (if any) among all samples. Four-point probe was used to measure the resistivity of the samples at room temperature. Magnetization measurements were carried out to determine the superconducting behavior (if any) of these samples.

Specific heat measurements from around 0 to 150 K were performed by using PPMS with zero magnetic field. The same samples as used for magnetization measurements were cut into cube shape of approximately 2 mm in edge length for these specific heat measurements.

Results and discussion

Powder X-ray diffraction patterns (Fig. 1) show all samples to be single-phased with tetragonal structure (space group P4/mmm) since all peaks could be identified. This reveals that such doping does not change the structure of these samples. Hence, any phenomenon that may occur in this study is assumed to be irrelevant to the structure change among the samples. On the other hand, it may disrupt the intrinsic properties of these samples. The calculated lattice constants are shown in Table 1. The values in brackets are samples doped with Ni and the rest are samples doped with Zn unless x=0 is sample without any dopant. Results show slight decrease in a and b-lattice constant after doped with Zn and Ni. The decrease is more obvious in c-lattice constant for both Zn and Ni-doped samples from x=0 until x=0.07. However, c-lattice constant increases for x=0.1 for both

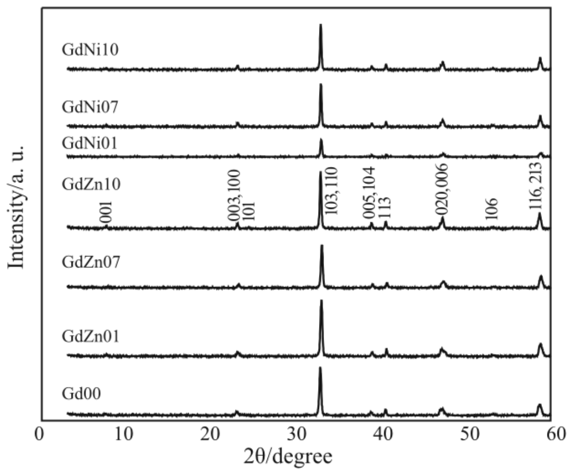

Fig. 1 X-ray powder diffraction patterns of $GdBaSrCu_3O_{7-\delta}$ (Gd00), $GdBaSrCu_{2.99}Zn_{0.01}O_{7-\delta}$ (GdZn01), $GdBaSrCu_{2.93}Zn_{0.07}O_{7-\delta}$ (GdZn07), $GdBaSrCu_{2.9}Zn_{0.1}O_{7-\delta}$ (GdZn10), $GdBaSrCu_{2.99}Ni_{0.01}O_{7-\delta}$ (GdNi01), $GdBaSrCu_{2.93}Ni_{0.07}O_{7-\delta}$ (GdNi07) and $GdBaSrCu_{2.9}Ni_{0.1}O_{7-\delta}$ (GdNi10)

Table 1 Resistivity at room temperature (ρ(300 K)), lattice constants (a, b, c), critical temperature (T_c) and Debye temperature at T around 10 K (Θ_D) of GdBaSr($Cu_{3-x}M_x$)$O_{7-\delta}$ samples (M=Zn and Ni)

Doped content x	ρ(300 K)/mΩ cm	Lattice constant/Å		T_c/K	Θ_D/K
		a=b	c		
0	1.18	3.854±0.004	11.571±0.007	85±1	297.5±0.5
0.01	1.30 (3.35)	3.837±0.003 (3.840±0.004)	11.550±0.006 (11.549±0.007)	81±1 (82±1)	293.9±0.5 (291.3±0.3)
0.07	1.34 (6.48)	3.837±0.003 (3.843±0.003)	11.517±0.005 (11.532±0.005)	53±1 (69±1)	289.5±0.3 (282.5±0.4)
0.1	5.12 (7.93)	3.846±0.003 (3.845±0.004)	11.542±0.005 (11.541±0.007)	– (65±1)	291.0±0.2 (279.4±0.4)

#The values in brackets are samples doped with Ni and the rest are samples doped with Zn unless x=0 is sample without any dopant

Zn and Ni doping (but still less than x=0 sample). The decrease in lattice constants is assumed to be related to the effect of different ionic radius of Cu, Zn and Ni. Hence, the CuO_2 plane may play an important role in the mechanism of superconductivity.

Scanning electron micrographs (SEM) of the internal section of the $GdBaSrCu_{2.99}Zn_{0.01}O_{7-\delta}$ sample (one of the samples' micrograph in which taken as example here) is shown in Fig. 2. The micrograph shows the existence of voids and pores indicating the degree of porosity of the sample. However, there is no significant variation in microstructure among all the samples as observed by SEM. In addition, measured density of samples were determined as 4.65±0.03 g cm^{-3} for $GdBaSrCu_3O_{7-\delta}$ sample, 5.20±0.04, 5.57±0.04 and 6.22±0.05 g cm^{-3} for Zn-doped samples with x=0.01, 0.07 and 0.1, respectively. For Ni-doped samples, measured density of samples were 4.47±0.03, 4.23±0.03 and 4.32±0.03 g cm^{-3} with x=0.01, 0.07 and 0.1, respectively. On the other hand, the relative density (measured density divided by ideal density calculated from lattice constants) was 0.70±0.01 for $GdBaSrCu_3O_{7-\delta}$ sample. For Zn-doped samples with x=0.01, 0.07 and 0.1, relative density were 0.78±0.01, 0.83±0.01 and 0.94±0.01, respectively. The relative density for Ni-doped samples with x=0.01, 0.07 and 0.1 were 0.67±0.01, 0.63±0.01 and 0.65±0.01, respectively.

The temperature dependence of magnetization of these polycrystalline samples are shown in Fig. 3. Results show that both Zn and Ni doping suppress the T_c of these samples. $GdBaSrCu_3O_{7-\delta}$ sample shows T_c at 85 K. For the Zn and Ni-doped sample with doping content of x=0.01, the T_c decreases to 81 and 82 K, respectively. Subsequently, for x=0.07 of Zn and Ni doping, the T_c decreases to 53 and 69 K, respectively. It is no longer a superconducting material for x=0.1 sample doped with Zn. Magnetization measurement reveals a T_c of around 65 K for x=0.1 sample doped with Ni but it seems like appeared as mix-phases (superconducting and non-superconducting phase) since the magnetization is not sharp and lower compared with others. However, it shows that Zn doping (as non-magnetic disturbance) suppresses the T_c more significantly compared with Ni doping (as magnetic disturbance). Decreasing of T_c is related to the disruption of spin correlation of the antiferromagnetic CuO_2 planes and it is suggested that Zn doping as a non-magnetic dopant might induce more unpaired hole carriers compared with Ni doping. Previous report [8] showed that Zn doping decreased the O p holes and increased the Cu d holes locally which is disadvantageous for superconductivity.

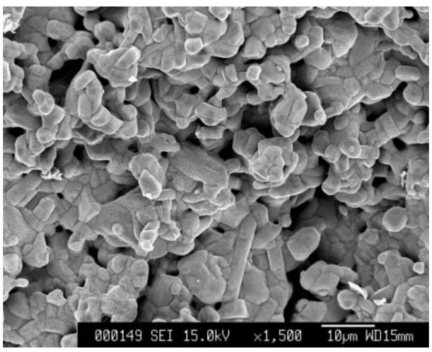

Fig. 2 SEM of $GdBaSrCu_{2.99}Zn_{0.01}O_{7-\delta}$ sample

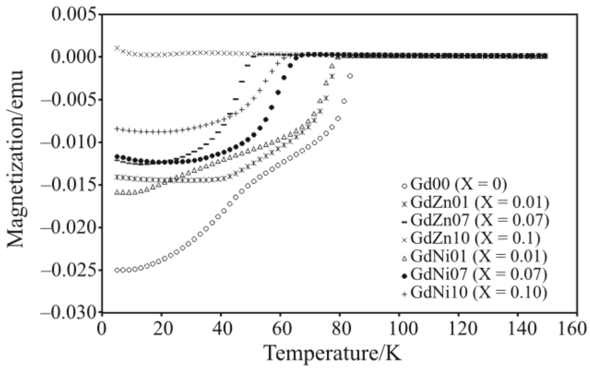

Fig. 3 Temperature dependence of magnetization for $GdBaSrCu_3O_{7-\delta}$ (Gd00), $GdBaSrCu_{2.99}Zn_{0.01}O_{7-\delta}$ (GdZn01), $GdBaSrCu_{2.93}Zn_{0.07}O_{7-\delta}$ (GdZn07), $GdBaSrCu_{2.9}Zn_{0.1}O_{7-\delta}$ (GdZn10), $GdBaSrCu_{2.99}Ni_{0.01}O_{7-\delta}$ (GdNi01), $GdBaSrCu_{2.93}Ni_{0.07}O_{7-\delta}$ (GdNi07) and $GdBaSrCu_{2.9}Ni_{0.1}O_{7-\delta}$ (GdNi10)

Specific heat measurements were carried out with thermal relaxation technique using PPMS and the results are shown in Fig. 4. Figures in the inset show the enlargement of linear relationship at low temperature and specific heat jump observed (if any) for each sample. Measurements were done in zero magnetic field to investigate and compare the effect of Zn as non-magnetic impurity and Ni as magnetic impurity on this HTSC sample. Measurements were taken from around 0 to 150 K but it was difficult to obtain $C_p(T)$ at the temperature below 6 K because of the Schottky like anomaly caused by splitting of the Gd^{3+} ions ground state due to crystal field effect and such anomaly is usually observed in most of the high temperature superconductors [9, 10].

The specific heat jump that observed around T_c clearly shows the second order phase transition of these samples. This specific heat jump is related to the difference between the specific heat of electronic contribution and the specific heat of superconducting state which has confirmed the bulk nature of HTSC. Such specific heat jump is shifted to lower temperature upon Zn and Ni doping and it is parallel to the decreasing of T_c. This specific heat jump is not obvious for $GdBaSrCu_{2.9}Ni_{0.1}O_{7-\delta}$ sample and disappeared for $GdBaSrCu_{2.9}Zn_{0.1}O_{7-\delta}$ sample (non-superconducting material). Furthermore, the magnitude of specific heat jump that observed is reducing upon the

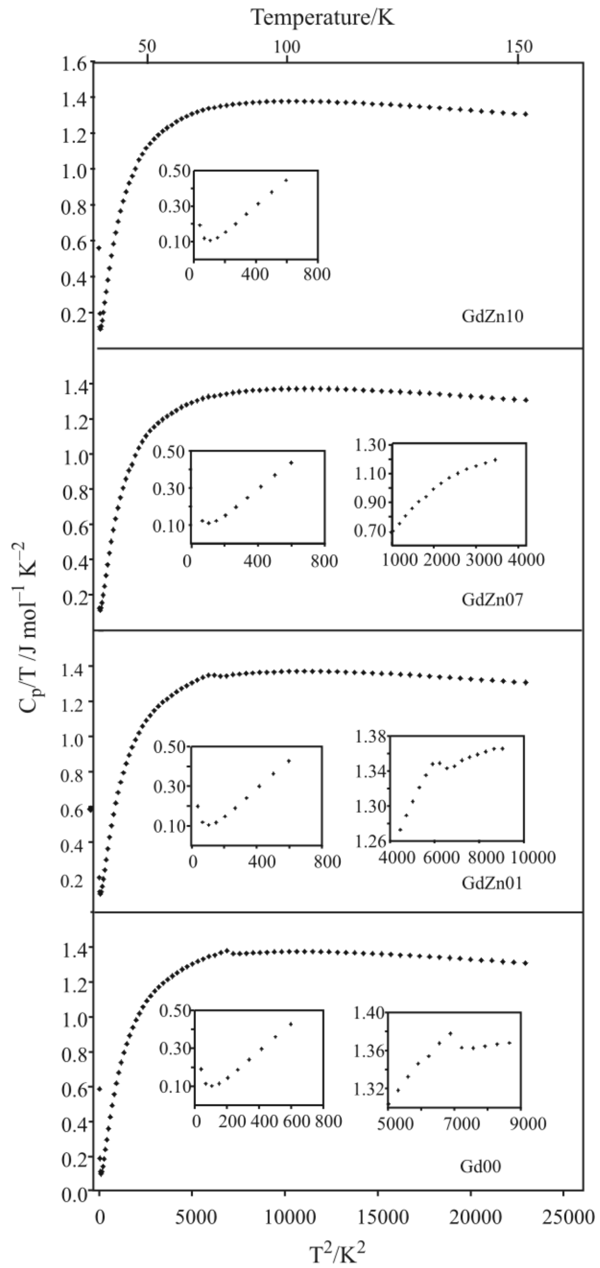

Fig. 4a Temperature dependence of specific heat (C_p/T) for $GdBaSrCu_3O_{7-\delta}$ (Gd00), $GdBaSrCu_{2.99}Zn_{0.01}O_{7-\delta}$ (GdZn01), $GdBaSrCu_{2.93}Zn_{0.07}O_{7-\delta}$ (GdZn07) and $GdBaSrCu_{2.9}Zn_{0.1}O_{7-\delta}$ (GdZn10)

decreasing of T_c which indicates a smaller density of state of electronic states since the superconductivity has been destroyed by Zn and Ni doping. The elimination of specific heat jump in this study is not due to the degree of homogeneity or porosity since XRD and SEM show no variation in structure and morphology for all samples.

Debye temperature, Θ_D at T around 10 K of each sample was calculated according to the Debye model by the following equation and the results are shown in Table 1.

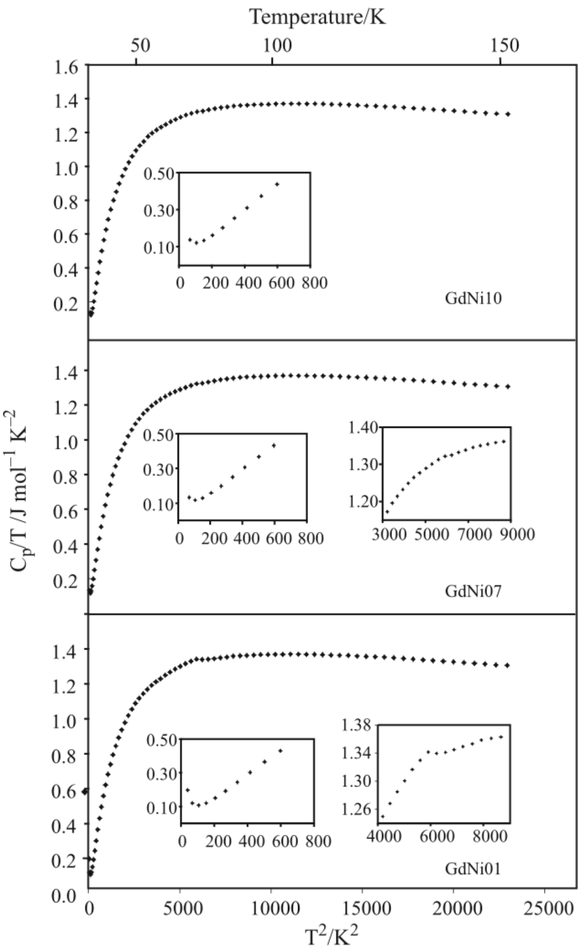

Fig. 4b Temperature dependence of specific heat (C_p/T) for $GdBaSrCu_{2.99}Ni_{0.01}O_{7-\delta}$ (GdNi01), $GdBaSrCu_{2.93}Ni_{0.07}O_{7-\delta}$ (GdNi07) and $GdBaSrCu_{2.9}Ni_{0.1}O_{7-\delta}$ (GdNi10)

$$\frac{C_p}{T} = n\frac{12\pi^4 R}{5\Theta_D^3}T^2$$

where n is the number of atoms per molecule and R is the gas constant (8.315 J mol^{-1} K^{-1}). However, the calculated Θ_D is strongly depended on the temperature and it is similar as in the case of YBCO sample that reported by Junod *et al.* [11]. At low temperature $T<\Theta_D/10$, results show that $C_p(T)\approx\beta T^3$ and hence, it is considering that lattice vibrations or phonons play a major role in these high temperature superconductors. Besides, calculations show that Θ_D is directly proportional to the T_c (for the effect of both dopants) in the superconducting materials. This coincides well with the results of YBCO compound [12, 13] and it would be some interactions between Θ_D and T_c in which may provide important information of the mechanism of superconductivity. As discussed before, the critical temperature, T_c is suppressed more obviously by Zn doping compared with Ni doping, but the Debye temperature, Θ_D for the samples doped with Ni is decreased more than the samples doped with Zn with same doping content. It may due to the correlation between Debye temperature and unpaired hole carriers. However, further investigation need to be carried out to determine the relationship between Debye temperature, critical temperature and hole carriers as well.

Conclusions

In summary, we report the effects of Zn and Ni doping on $GdBaSrCu_3O_{7-\delta}$ samples and their properties through specific heat measurements. The critical temperature is decreasing with increasing of both Zn and Ni doping contents. The specific heat jump that observed around T_c clearly shows the second order phase transition of these samples. Such specific heat jump is shifted to lower temperature upon Zn and Ni doping parallel to the decreasing of T_c. Debye temperature, Θ_D (derived from specific heat measurements) calculated at around 10 K is found to be directly proportional to the T_c in superconducting materials. Besides, at low temperature in which $T<\Theta_D/10$, results show that $C_p(T)\approx\beta T^3$. Hence, it is considering that lattice vibrations or phonons play a major role in these high temperature superconductors.

Acknowledgements

This work has been partially supported by The Japan Science Society under the Sasakawa Scientific Research Grant. T. V. Chong wish to thank Rotary Yoneyama Memorial Foundation for the scholarship of study.

References

1 E. Takayama-Muromachi, Y. Uchida and K. Kato, Jpn. J. Appl. Phys., 26 (1987) L2087.
2 J. L. Tallon, C. Bernhard, G. V. M. Williams and J. W. Loram, Phys. Rev. Lett., 79 (1997) 5294.
3 A. V. Mahajan, H. Alloul, G. Collin and J. F. Marucco, Phys. Rev. Lett., 72 (1994) 3100.
4 H. Alloul, J. Bobroff and P. Mendels, Phys. Rev. Lett., 78 (1997) 2494.
5 A. Lanzara, P. V. Bogdanov, X. J. Zhou, S. A. Kellar, D. L. Feng, E. D. Lu, T. Yoshida, H. Eisaki, A. Fujimori, K. Kishio, J.-I. Shimoyama, T. Noda, S. Uchida, Z. Hussain and Z.-X. Shen, Nature, 412 (2001) 510.
6 G. M. Zhao, H. Keller and K. Conder, Unconventional Isotope Effects in the High-Temperature Cuprate Superconductors, cond-mat/0204447 (2002).
7 R. Abd-Shukor, Supercond. Sci. Technol., 15 (2002) 435.
8 X. J. Hao, Y. S. Zhou, L. Y. Zhang and H. Y. Wang, Mod. Phys. Lett. B, 8 (10) (1994) 641.
9 N. V. Tristan, S. A. Nikitin, T. Palewski, K. Nenkov and K. Skokov, J. Magn. Magn. Mater., 258–259 (2003) 583.
10 H. Gao, Y. Wang, L. Shan, X. Yao and H. H. Wen, Physica C, 432 (2005) 293.
11 A. Junod, D. Eckert, T. Graf, E. Kaldis, J. Karpinski, S. Rusiecki, D. Sanchez, G. Triscone and J. Muller, Physica C, 168 (1990) 47.
12 L. K. Aminov, V. A. Ivanshin, I. N. Kurkin, M. R. Gafurov, I. Kh. Salikhov, H. Keller and M. Gutmann, Physica C, 349 (2001) 30.
13 H. Ledbetter, Physica C, 235–240 (1994) 1325.

DOI: 10.1007/s10973-007-8964-0