

Effect of Ga and Zn doping on coherent transition of YBCO superconductor

A Mohanta & D Behera*

Department of Physics, National Institute of Technology, Rourkela, 769 008

*E-mail: dhrubananda_behera@yahoo.in

Received 3 February 2009; revised 1 June 2009; accepted 13 July 2009

The simultaneous incorporation of Ga^{3+} and Zn^{2+} to the Cu-site of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ has been analyzed for microstructural and electrical properties. Temperature-dependent electrical resistivity, X-ray diffraction and SEM analysis of a set of $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ films prepared by solid state reaction technique have been investigated to study the substitutional effects of Ga and Zn at chain and plane site of Cu, respectively. The redistribution of charges in the superconducting system due to oxygen content and the resistance of the weak-links related inhomogeneities give rise to T_c degradation and dual values of exponents in the T_{c0} region. The exponent values for fluctuation conductivity in the T_{c0} region decrease with increase of substitution concentration. The dual exponent character shows that the intergranular weak links develop more resistance with increasing impurities.

Keywords: Superconductors, Excess conductivity, Coherence transition

1 Introduction

The planar character and granularity of the system is the characteristic properties for determining superconducting parameters. The electronic properties of copper oxide superconductors change with doping at chain and plane sites with iso and aliovalent ions^{1,2}. To have an understanding of the mechanism of superconductivity a deep insight to the electronic properties is essential. The control of charge carriers and oxygen content has a crucial effect on superconducting properties³. Charge fluctuations and anti-ferromagnetically coupled spin fluctuations are influenced by substitution of metal ions at the Cu site or by the removal of oxygen from the structure². Zinc substitution changes the charge on O^{2-} site and modulates its position. It plays a detrimental effect on interlayer charge transfer which also leads to the degradation of superconductivity⁴. The mechanism for the reduction of T_c in Zn doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ (YBCO) could be because of local structural disorder induced by zinc sites, breakdown of hole pairs by Zn sitting either in the CuO_2 planes or in between the CuO_2 planes⁵. Zn doping creates in-plane disorder without affecting the hole-density. The presence of spinless divalent ion like Zn in the planes destroys long range order of spin system and leads to strong changes of the superconducting parameters in the vicinity⁶. It has been established that Cu(2) site substitution lead to formation of magnetic moments which become pair breakers⁷. Zn substituted compounds were more oxygen deficient as compared

to Zn free ones⁸. The mechanism for T_c suppression in Zn doped samples is strictly electronic in nature. This T_c decrease is reported⁷ to be linear with $dT_c/dx \sim 10 \text{ K/ at } \%$ and $\sim 8 \text{ K/ at } \%$ of Zn. Zn doping shows the highest depression rate, followed by Ni, Ga and Co doping. This is because of the fact that Zn and Ni substitute at Cu (2) sites on CuO_2 planes in the lattice, whereas Co and Ga occupy Cu (1) sites along Cu-O chains and they have different magnetic moments.

Ga^{3+} impurities have a five-fold co-ordination. The Cu atoms in the Cu-O chains have a 4-fold co-ordination. So there exists a coordination mismatch between the parent and the dopant. Rodriguez *et al.*⁹ have reported that Cu (1) site substitution affects the superconductivity mainly through a decrease in P type carriers in CuO_2 planes⁷ and decreases T_c at a rate 2-5 K/ at %. When Ga and Zn ions are substituted for Cu, they apparently have a site preference maintaining an orthorhombic structure. The simultaneous substitutions of Cu by Ga and Zn with +3 and +2 charge state respectively have been analyzed². The reduction of T_c and orthorhombic distortion when Ga and Zn ions are present together, suggest interplay between the local magnetic moments which appear as a consequence of the doping of lattice at both the sites². Inhomogeneities strongly influence the region, where the zero resistance state is approached from above. The microscopic inhomogeneities such as structural defects (twin boundaries, stacking faults) and

chemical imperfections (oxygen deficiencies) occur inside the grains. The length scale of these inhomogeneities is smaller than that of the mesoscopic inhomogeneities, but still larger than coherence length (ξ).

In the present paper, the behaviour of chain and plane sites in the coherence region of YBCO superconductor structures has been studied. The exponents at the tailing region and the influence of inhomogeneities on their microstructures are studied to contribute to a better understanding of the nature of superconductivity for these compounds.

2 Experimental Details

A series of polycrystalline samples of $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ ($x = 0, 0.012, 0.025$) and Yttrium Barium Copper Oxide (YBCO) have been prepared by the standard solid-state reaction method from the appropriate amounts of high-purity powders of constituent oxides and BaCO_3 in the required proportions. Calcinations of the mixture was done at 850°C in air and cooled to room temperature over a period of 10 h. This process of heating and grinding was carried out four times. Finally the samples were pressed into pallets and sintered at 880°C for 12 h annealed at 450°C for 10 h in oxygen atmosphere and cooled to room temperature over a period of 10 h. All the samples were characterized by the X-ray powder diffraction technique using a Philips analytical X-ray instrument, X' Pert-MPD (PW 3020 vertical goniometer and 3710 mpd control unit) employing Bragg-Brentano para-focusing optics. Line focus Ni-filtered CuK_α from an X-ray tube (operated at 40 kV and 30 mA) was collimated through soller slit (SS) of 0.04° , fixed divergence slit of 1° and mask (5 mm) before getting it diffracted from the sample. Experimental control and data acquisition were fully automated through computer. Diffraction patterns of the samples showed that they were single phase with an impurity level of less than 1%.

Superconducting transition temperatures were determined by resistivity measurements. The temperature dependent resistance, $R(T)$ was measured using four-probe technique with a nanovoltmeter (Keithley-181) and an indigenously developed constant current source. With the voltage resolution of 10^{-7} V of the nanovoltmeter, a constant current of 1 mA flowing through the samples gives a resolution $\sim 1 \mu\Omega$ in the measured resistance. A closed cycle helium refrigerator (APD cryogenics-HC2) and a temperature controller (Scientific Co. 9600-1) were

used for temperature variation. The temperature controller used a Si diode sensor having a temperature resolution of ± 0.1 K. A computer controlled data acquisition system was used to acquire the resistance data from 40 K to room temperature. Resistance data were acquired during the heating cycle with heating rate confined to 3 K per min.

The grain morphology of the fractured surface of the samples was analyzed by scanning electron microscope (Model No JSM-6480 LV, Make JEOL). Compositional analysis was determined by energy dispersive X-ray analysis (EDX) using an INCA Oxford analyzer attached to a scanning electron microscope.

3 Results and Discussion

The XRD patterns of all the samples $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ ($x = 0, 0.012, 0.025$) and YBCO shown in Fig. 1 were indexed in the orthorhombic phase with space group $Pmmm$. All the samples were found to be monophasic without impurity like BaCuO_3 . The lattice parameters and unit cell volumes of these samples are presented in Table 1. It may be noticed from the Table 1 that the lattice parameter a increases while b remains almost constant and c parameter does not change much with increase in Ga doping (XRD). The major YBCO peak at $2\theta = 32.7$ increases with Ga wt % and other impurity peaks get reduced. This is also confirmed analysis by EDX. This analysis shows that, even in the low-concentration doped samples, substituents reside within the grains.

The orthorhombic distortion $\delta = 2(b-a)/(b+a)$ and variation of orthorhombicity $(b-a)/a$ decreases with Ga^{3+} concentration (Table 2). Particle sizes for all the

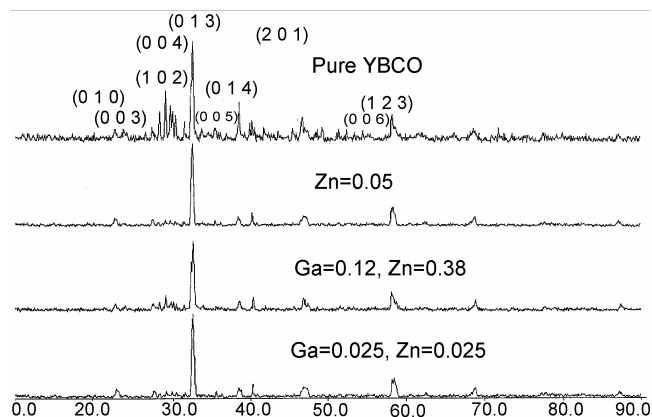


Fig. 1 — XRD pattern for YBCO and $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ with: (1) Ga = 0.0 and Zn = 0.05, (2) Ga = 0.012 and Zn = 0.038, (3) Ga = 0.025 and Zn = 0.025

Table 1—Lattice parameters and unit cell volumes of the samples, Pure YBCO, $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ ($x = 0.0, 0.012, 0.025$) i.e. Ga = 0.0 and Zn = 0.05, Ga = 0.012 and Zn = 0.038, Ga = 0.025 and Zn = 0.025

Sample	a (Å)	b (Å)	c (Å)	Volume (Å ³)
YBCO	3.8273	3.8882	11.6859	173.90147
Ga = 0, Zn = 0.05	3.8293	3.8864	11.6832	173.87162
Ga = 0.012, Zn = 0.038	3.8294	3.8857	11.6856	173.87601
Ga = 0.025, Zn = 0.025	3.8315	3.8899	11.6853	174.15948

Table 2—Orthorhombic distortion (δ), variation of orthorhombicity, particle size (t) of pure YBCO and $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ ($x = 0.0, 0.012, 0.025$)

Sample	$\delta = \frac{2(b-a)}{b+a}$	$\frac{b-a}{a}$	Crystallite Size (t) in μm
YBCO	0.015786	0.0159	0.1712
Ga = 0, Zn = 0.05	0.01490	0.0149	0.1865
Ga = 0.012, Zn = 0.038	0.0146208	0.0147	0.17465
Ga = 0.025, Zn = 0.025	0.014867	0.0152	0.17463

Ga, Zn doped samples are of the same order that of YBCO. The Zn doped sample has the orthorhombic distortion (δ) less than undoped YBCO system. The structure of YBCO basically dictated by oxygen ordering^{1,3,8} and the charge state of Cu(1) ions³ in Cu-O chains. The above results on structural changes due to incorporation of Zn and Ga indicates that Zn preferentially substitutes^{10,11} for Cu(2) at the plane site where it does not affect either oxygen vacancy ordering or the charge state of Cu(1) ions and Ga substitutes for Cu(1) at the chain site where it can affect both. Sugai *et al.*¹² have mentioned that oxygen in the Cu-O chain of Ga-doped YBCO is more stable than that of undoped one. Since the formal charge state of Cu and oxygen vacancy ordering are intimately linked the subtle structural change from orthorhombic to tetragonal with increasing Ga³⁺ concentration is probably electrically driven² by Cu²⁺.

The scanning electron microscopic (SEM) images of the prepared samples are shown in Fig. 2. This picture depicts that the average grain size decreases with decrease in Zn concentration and from the alignment of the grains it is assumed that the segregation of grains decreases with simultaneous substitution of Ga and Zn. In terms of their contribution to the total volume, the mean grain diameters were around 2 μm . From the surface morphology of the samples, a good homogeneity and

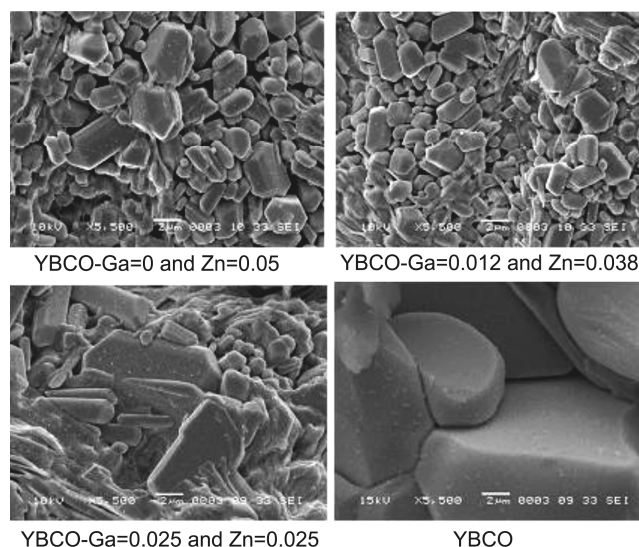


Fig. 2—SEM images of YBCO and Zn and Ga doped samples of $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ with: (1) Ga = 0.0 and Zn = 0.05, (2) Ga = 0.012 and Zn = 0.038, (3) Ga = 0.025 and Zn = 0.025

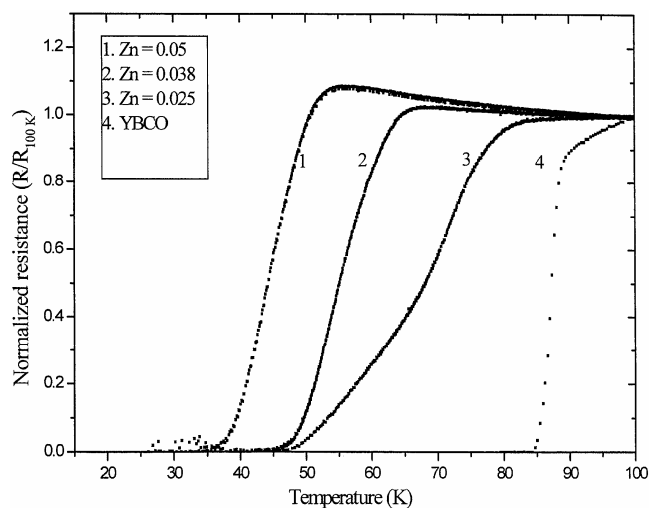


Fig. 3—Temperature dependent resistance of YBCO and with varying Zn and Ga concentration in $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ compounds with: (1) Ga = 0.0 and Zn = 0.05, (2) Ga = 0.012 and Zn = 0.038, (3) Ga = 0.025 and Zn = 0.025 and YBCO.

epitaxy can be inferred. These observations reveal a smooth grain-surface without significant impurities. The metal ionic substitution at the Cu site of YBCO does not affect grain boundaries, as it goes into the grain.

The temperature dependence of resistivity (ρ) for $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ compounds with varying Zn and Ga concentration is shown in Fig. 3. Sample $x=0$ (Zn = 0.05 and Ga = 0.0) shows a semiconducting type ($d\rho/dT < 0$) temperature dependence of resistivity

from 300 K down to the onset of superconductivity transition which is in agreement with earlier studies^{2,3}. Furthermore, the change in electronic state produced by Zn^{2+} may be the main reason why superconductivity is depressed by zinc doping so strongly (Fig. 3). Zinc doping does not change the overall carrier hole density but it gives rise to a redistribution of charges that produces strong electron scattering not only from Zn^{2+} but also from nearby sites which breaks the cooper pairs and therefore decreases T_c rapidly^{2,3}. The T_c of YBCO system containing both Zn^{2+} and Ga^{3+} is lower than the expected value based on interpolation between Zn doped Ga samples².

From the Table 3 it may be concluded that, the T_{c0} value decreases with increase in Zn concentration. Zn substitutes Cu(2) sites more preferably i.e., CuO_2 planes are substituted preferentially than chains. Therefore, strong changes in the electronic state as well as superconducting properties are expected with the increasing Zn content in these planes. In Zn doped YBCO samples, it has been observed that the Zn doping creates in-plane disorder without affecting the hole density^{4,14}. Therefore, the T_c values decrease with increase in Zn concentration and the observed resistance is less than that of the Pure YBCO sample. The Ga^{3+} substitutes Cu preferentially at the chain site. The substituted Ga, a trivalent, is known to assimilate extra oxygen¹⁴ into the CuO_2 planes where the actual superconduction occurs is not directly affected¹⁵. Therefore, T_c is not affected by Ga^{3+} as much as it is affected by doping Zn^{2+} which preferentially substitutes Cu at the plane site. Incorporation of Zn^{2+} in CuO_2 planes, which is a non-magnetic and stable 2+ ion, disturbs the antiferromagnetically coupled spin fluctuations in the plane. The hopping of electrons from chain to plane “proximity coupling”, has been suggested by Chen and Hirschfeld¹⁶. The reduction of T_{c0} (Table 3) and orthorhombic distortion when simultaneous doping of Ga and Zn is done suggests an interplay between the local magnetic moments which appears as a

consequence of the doping of the lattice at both sites.

The system is granular in nature having two components, first the superconducting grains and the second the Josephson weak links. In the tailing region close to T_{c0} , the superconducting grains and the grain boundary weak links through which superconductivity is established through Josephson tunneling is shown in Fig. 3. The second component consists of weak links which are not superconducting, either due to the link being too weak or due to the measuring current of the corresponding link or the temperature being higher than the T_c of that link. For $T < T_{c0}$, the first component provides the channel for the transport of supercurrent. For $T_{c0} < T < T_c$, the volume of the first component is not adequate enough to provide a percolative path for super current and the R - T transition shows a tail with $R \neq 0$. Only when $T \leq T_{c0}$, a percolative path through the first component is established and a global superconductivity is achieved in the sample with R going to zero. First superconductivity sets in within the grains and at somewhat lower temperature long-range superconducting order takes place over the whole sample¹⁷. Just before falling to zero value the resistive transition abruptly changes drastically the slope and achieves zero resistance, only after a long and flat tail¹⁸.

In the temperature close to T_{c0} , attempts have been made to fit the resistance to a power law of the form:

$$R = A \epsilon_0^\delta \quad \dots (1)$$

where, ϵ_0 is the reduced temperature, $T - T_{c0}/T_{c0}$ and δ are the exponent (Fig. 4). The exponent for fluctuation conductivity and the relevant critical temperature, T_{c0} , which is close to the point where resistivity vanishes, has been observed¹⁹. For YBCO samples before the resistance attains zero value indicates that the superconducting grains get progressively coupled to each other by Josephson tunneling across the grain boundary weak links and the onset of global superconductivity in these samples is effected only when a percolative superconducting path is established through these links²⁰.

The region of approach to the zero resistance state reveals the occurrence of a coherence transition at a lower temperature. Focus is on the coherence transition, where the phases of the order parameter in individual grains become long-range ordered and the zero-resistance state sets in. This transition is related to the connective nature of the granular samples and is controlled by fluctuations of the order-parameter

Table 3 — Variation of resistance at 100 K and transition temperatures pure YBCO and $\text{YBa}_2(\text{Cu}_{0.95}\text{Zn}_{0.05-x}\text{Ga}_x)_3\text{O}_{7-y}$ ($x = 0.0, 0.012, 0.025$)

Samples	T_{c0} (K)	T_c (K)	$R_{100\text{ K}}$ (Ohm)
Pure YBCO	84.3	88.7	0.015
Ga = 0.025, Zn = 0.025	47.47	83.5	0.044
Ga = 0.012, Zn = 0.038	46.0	65.2	0.031
Ga = 0, Zn = 0.05	36.0	56.2	0.059

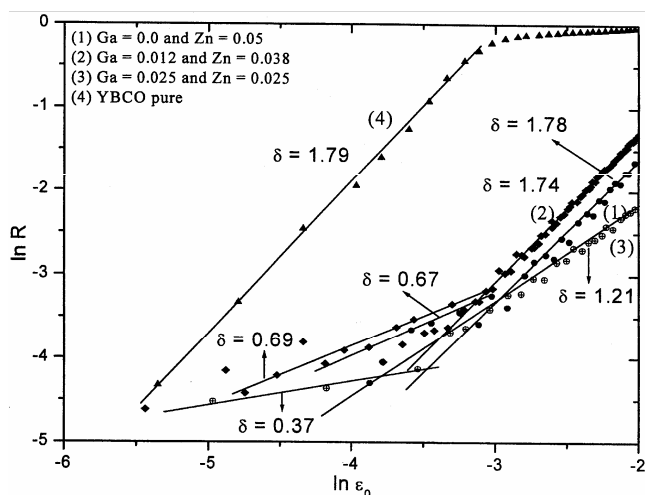


Fig. 4 — Logarithmic plot of resistance as a function of reduced temperature showing their exponents: (1) Ga = 0.0 and Zn = 0.05, (2) Ga = 0.012 and Zn = 0.038, (3) Ga = 0.025 and Zn = 0.025, (4) YBCO pristine

phase of individual grains. The electric resistivity falls steeply as a function of temperature. However, just before falling to zero the samples show exponent for fluctuation conductivity. The δ value obtained for pure YBCO is 1.79. This finding gives strong support to the interpretation of the coherence transition as a genuine critical phenomenon.

The occurrence of two values of δ may be due to weak-link related dissipation organized as a global percolation. Besides the trivial dependence of normalized resistance on sample inhomogeneities the microstructural features of the sample such as average grain size plays an important role towards the existence of two δ values. Exponents in the tailing region are obtained, may be due to the resistance of the weak links which are in a resistive state. Such a resistive state may be produced by penetration of mobile fluxoids in weak superconducting regions²¹ or, if the weak links are considered as Josephson junctions, by a transition to a resistive state of these junctions when the thermal energy exceeds the Josephson coupling energy.

4 Conclusions

The doping effect of Ga and Zn on the microstructural and electrical properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$ has been reported. The transition temperature has been found to decrease with increasing Zn doping, while an abrupt increase in resistance is noticed on doping an equal amount Zn and Ga wt.%. The average grain size is also found to decrease with decrease in Zn concentration. From the

study it is concluded that the presence of Zn^{2+} in the CuO_2 planes breaks the coupling between cooper pairs and hence affects superconductivity in YBCO type systems. Ga^{3+} on the other hand indirectly affects the superconductivity by decreasing the carrier concentrations in the CuO_2 planes through reduction of the charge state of Cu ion from 3+ to 2+ in the Cu-O chains. Zinc doping gives rise to a redistribution of charges in the superconducting system which breaks the cooper pairs and decreases the oxygen content, therefore T_c decreases. With increase in Zn concentration both T_c and T_{c0} values decrease. T_c is not affected much by Ga^{3+} as much as it is affected by doping Zn^{2+} . The exponent values for fluctuation conductivity in the T_{c0} region decrease with increase of substitution concentration. The dual exponent character shows that the intergranular weak links develop more resistance with increasing impurities.

References

- 1 Rajneesh M K, Singh K, Bhattacharya S, Dixit M & Gaur N K, *Solid State Commun*, 141 (2007) 605.
- 2 Mishra N C, Rajarajan A K, Patnaik K, Vijayaraghavan R & Gupta L C, *Solid State Commun*, 75 (1990) 987.
- 3 Rodriguez M A, Navrotsky A & Licci F, *Physica C*, 329 (2000) 88.
- 4 Li Ang, Ying Xuenong, Xu Xiaoshan, *et al.*, *Physica C*, 337 (2000) 285.
- 5 Raj S, Dhal B B, Padhi H C, Behera D & N C Mishra, *Solid State Communications*, 105 (1998) 767.
- 6 Hussain M, Kuroda S & Takita K, *Physica C*, 297 (1998) 176.
- 7 Zhou Y X, Scruggs S & Salama K, *Supercond Sci Technol*, 19 (2006) 13.
- 8 Naqib S H, *Physica C*, 43 (2006) 443.
- 9 Rodriguez M A, Navrotsky A & F Licci, *Physica C*, 329 (2000) 88.
- 10 Walker D J C, Mackenzie A P & Cooper J R, *Phys Rev B*, 51 (1995) 15653.
- 11 Zhang X, Yip KW & Ong C K, *Physica C*, 234 (1994) 99.
- 12 Sugai S, Matsukawa Y, Shimosato K & Oda S, *Japan J Appl phys*, 39 (2000) L1032; Dogra Anjana, Rayaprol S, Shah N A & Kuberkar D G, *Modern Physics Letters B*, 18 (2004) 485.
- 13 Naqib S H, *Supercond Sci Technol*, 20 (2007) 964.
- 14 Song I H, Lee E H, Kim B M, Song I & Park G, *Appl Phys Lett*, 74 (1999) 2053.
- 15 Shkedy L, Koren G & Polturak E, ar Xiv: 0502254v1 (*cond-mat Supr-con*), 10 Feb. 2005.
- 16 Chen W and Hirschfeld P J, ar Xiv: 0811 4240v2 (*cond-mat Supr-con*), 27 Nov, 2008.
- 17 Vieira V N, Pureur P & J Schaf, *Phys Rev B*, 66 (2002) 224506.
- 18 Diasa F T, Vieira V N, Rodrigues Jr P, *et al.*, *Physica C*, 408 (2004) 688.
- 19 Jurelo AR, Abrego-Castillo I, Roa-Rojas J, *et al.*, *Physica C*, 311 (1999) 133.
- 20 Behera D & Mishra N C, *Supercon Sci Technol*, 15 (2002) 72.
- 21 Song Y, Mishra A, Crooker P P & Gaines J R, *Phys Rev Lett B*, 45 (1992) 7574.