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# Harmonic generation in superconducting Bi(Pb)SrCaCuO thick films

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**Abstract.** We present a detailed study of harmonic generation in Bi(Pb)SrCaCuO superconducting thick film prepared by screen printing technique. A comparative study of amplitude of harmonics of two films of different $J_c$ have been carried out. The variation of amplitudes of the harmonics are studied as a function of magnitude of ac and dc field. The temperature dependence of amplitude of third harmonic ($V_3$) is studied with increasing amplitude as well as frequency of ac field. These results are analyzed in the frame work of critical state model. $V_3$-$T$ curve also indicates the presence of two phases in Bi(Pb)SrCaCuO film.

**Keywords.** Harmonic generation; high temperature superconductors.

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## 1. Introduction

There has been a lot of interest in studying high $T_c$ superconductors in presence of external ac and dc magnetic fields [1–11]. When an applied ac field ($H_{ac}$) of frequency $f$ exceeds $H_{c1}$, the magnetic flux starts penetrating into high-$T_c$ superconductor and its magnetic response become non-linear due to flux pinning effect. A direct consequence of non-linearity in the magnetization is the generation of higher odd harmonics of frequency $(2n + 1)f$. The application of dc field in addition to ac field causes generation of even harmonics also. The harmonic generation effect is observed till the sample is in superconducting state. The magnitude of odd harmonics increases as the $H_{ac}$ is increased. The absence of even harmonics at zero dc field indicates the symmetry of hysteresis loop. The critical state model of Bean [2] which assumes the local critical current independent of field, gives the first analysis of the generation of odd harmonics. The extended critical state model which assumes the dependence of critical current upon the magnetic field has been used to explain the generation of even harmonics [3]. The application of dc field in addition to ac field, breaks the symmetry and leads to generation of even harmonics. Harmonic generation in bulk superconductors are reported by several workers [1,3,4,5,6]. Yamamoto *et al* [7] reported third harmonic generation in YBCO thin film prepared by evaporation technique.

Shaulov *et al* [8] showed the use of the third harmonic to investigate the multiphase nature of YBCO thin film. Khare *et al* [9] reported harmonic generation in laser ablated YBCO thin film. Revenaz and Dumas [10] reported harmonic generation due to magnetically modulated microwave absorption in YBCO thin film. Recently high-$T_c$ magnetic field sensor based on harmonic generation effect in Bi (Pb)SrCaCuO thick film has been reported [11].

In this paper, we report a detailed study of harmonic generation effects in Bi(Pb)SrCaCuO superconducting thick films with various combinations of ac and dc fields. The results are analyzed in the framework of critical state model.

## 2. Experimental details

Superconducting thick films of Bi(Pb)SrCaCuO have been prepared on single crystal MgO(100) substrate by screen printing technique. The details of the technique are described elsewhere [12]. The starting composition of the powders for printing was taken in the ratio of Bi:Pb:Sr:Ca:Cu = 1.7:0.4:2:2:3. High purity powders of $Bi_2O_3$, PbO, $SrCO_3$, $CaCO_3$ and CuO were thoroughly mixed, ground and calcined at 820° C for 24 hr in air. The fine calcined powder was mixed with cyclohexanol to form a paste which was screen printed onto MgO (100) substrates. The as-printed films were then heated at 300°C for 1 hr to remove the organic solvent. The films were further subjected to a post annealing treatment, consisting of heating the films in air at 860°C (10 min), 880°C (1 min), 860°C (10 min) and 840°C (80 hr), followed by slow cooling (5°C/min) to room temperature.

The electrical resistance was measured using four probe dc method. The critical current density of the films was measured by standard four probe method using 1 $\mu v$/cm criteria. X-ray diffraction pattern was recorded at room temperature using CuK$\alpha$ radiation.

Figure 1 shows the experimental set-up for observing harmonic generation effect in high-$T_c$ Bi(Pb)SrCaCuO films. A 25 turn flat coil (diameter 8mm) was glued on the backside

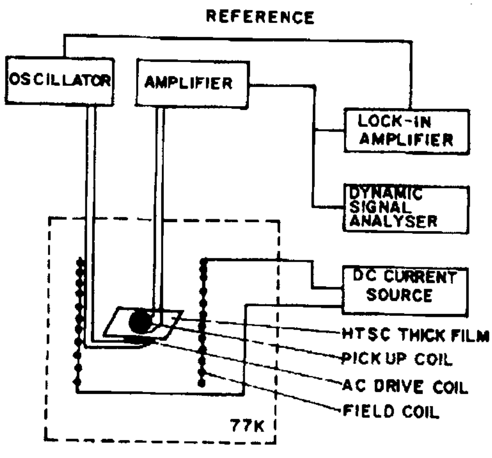


**Figure 1.** Schematic diagram of the experimental set-up used for observing the harmonic generation effect in a high-$T_c$ superconducting thick film.

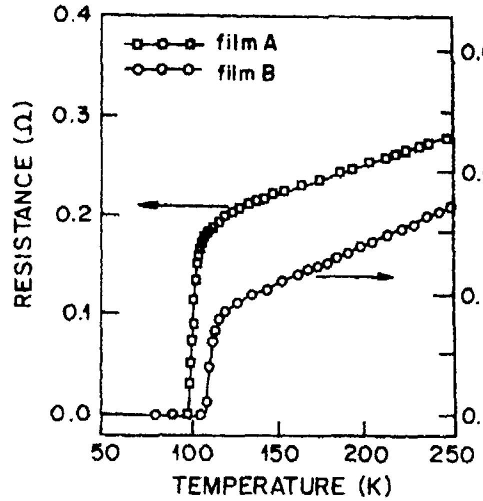


**Figure 2.** Resistance-temperature plot of thick films $A$ and $B$.

of the substrate for applying ac field through an oscillator. A flat coil of 25 turn (diameter 2mm) was glued on the surface of the film to pick-up signals from the film and was connected to a low noise amplifier. The output to the amplified signal was connected to a dynamic signal analyzer for observing the frequency spectrum of the pick-up signal. A solenoid of diameter 2.8 cm surrounding the film was used to apply dc field. Both ac and dc fields were applied perpendicular to the surface of the film. A lock-in amplifier was also used for measuring amplitude of the second harmonic signal.

## 3. Results and discussion

Figure 2 shows the temperature dependence of resistance of the two films A and B. Film A has $T_c(R = 0) = 97$K and the film B has $T_c(R = 0) = 107$K. $J_c$ ($T = 77$K) for film A and film B are found to be 45 A/cm$^2$ and 20 A/cm$^2$ respectively. XRD studies reveal that both films have mixture of 2212 and 2223 phases and these are preferentially oriented along the $c$-axis.

Figure 3 shows the frequency spectrum of the harmonic signal at pick-up coil for film A for two cases (a) $H_{ac} = 4.3$G, $f_{ac} = 10$ kHz, $H_{dc} = 0$, $T = 77$K and (b) $H_{ac} = 4.3$G, $f_{ac} = 10$ kHz, $H_{dc} = 0.45$G, $T = 77$K. It is evident from figure 3 that when an ac field is applied odd harmonics at frequencies 30, 50, 70 and 90 kHz are generated. When dc field is also applied in addition to an ac field, even harmonics at frequencies 20, 40, 60 and 80 kHz are also observed.

Figures 4 and 5 show the variation of the amplitude of the third harmonic, $V_3$, at 77K with $H_{ac}$ ($f_{ac} = 10$ kHz and $H_{dc} = 0$) for film A and B respectively. For film A, initially $V_3$ is zero and it starts growing when $H_{ac} > 0.7$G. The growth of $V_3$ is fast in the range of 0.7–3.0G and after $H_{ac}$ exceeds 3.5 G, it shows signs of saturation. For film B, initially $V_3$ is zero and it starts growing with $H_{ac} > 0.1$G. The growth of $V_3$ is fast in the range of 0.1–1.6G, and when $H_{ac}$ exceeds 2G, $V_3$, starts decreasing. These observations can

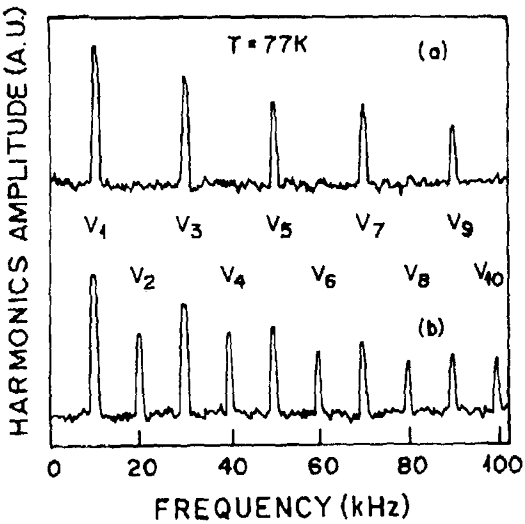


**Figure 3.** Frequency spectrum of the signal at pick-up coil for Bi(Pb) SrCaCuO thick film A: (**a**) $H_{ac}$ = 4.3G. $f_{ac}$ = 10 kHz, $H_{dc}$ = 0, $T$=77K (**b**) $H_{ac}$ = 4.3 G. $f_{ac}$ = 10 kHz, $H_{dc}$ = 0, $T$ = 77 K.

be understood in the framework of critical state model [3,4,9]. Higher harmonics will appear only when flux starts penetrating into the film. In the beginning, $H_{ac}$ is smaller than the critical field, $H_{c1}$, therefore higher harmonics are not observed. However, when $H_{ac}$ becomes larger than $H_{c1}, V_3$ starts growing. Increase of $H_{ac}$ above $H_{c1}$ increases the penetration of the flux and so $V_3$ keeps on growing. The present Bi(Pb)SrCaCuO films are polycrystalline in which superconducting grains are coupled with Josephson weak links. For films with larger $J_c$ means stronger Josephson coupling exists. For film, A, $J_c$ is higher. Thus, it can be expected that penetration of ac field occurs at higher value of $H_{ac}$ as observed experimentally. The growth of $V_3$ reaches to a saturation value when ac field approaches to the saturation field $H^*$ which is given as [13].

$$H^* = kJ_ca$$

where $k$ is a geometric constant, $J_c$ is the critical current density and $a$ is the dimension perpendicular to the field. For film A, $J_c$ is higher so, $H^*$ is higher and $V_3$ is expected to attain saturation at higher $H_{ac}$ and for film B having a lower value of $J_c$, $V_3$ is expected to attain saturation value at lower $H_{ac}$. This is in agreement with the observed behaviour. Critical state model predicts that for $H_{ac} > H^*$, the amplitude of higher harmonics will be proportional to $1/H_{ac}$. In film B, $H^*$ is small so when $H_{ac} > H^*$ (=1.7G), $V_3$ starts decreasing. For film $A, H^*$ is large so even up to $H_{ac}$ = 4.25G, we do not reach to the condition $H_{ac} > H^*$ and hence we do not observe any decrease in $V_3$.

Figures 6 and 7 show the variation of amplitudes of harmonics $V_2, V_3, V_4, V_5$ and $V_6$ with $H_{dc}$, keeping $H_{ac}$ constant at 4.3G and 1.7G for films A and B, respectively. When dc field ($H_{dc}$) is gradually increased the amplitude of even harmonics ($V_2$, $V_4$ and $V_6$) starts increasing, reaching a saturation value and then starts decreasing, while the amplitude of odd harmonics ($V_3, V_5$) decreases continuously, in both the films. The amplitude of even harmonics in film A is found to decrease when $H_{dc} > 1.7$G, whereas for film B, even

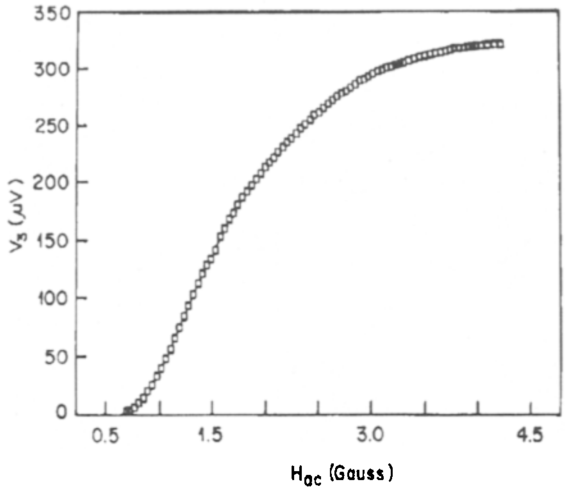


**Figure 4.** Variation of amplitude of the third harmonic ($V_3$) with $H_{\rm ac}$ at 77K ($H_{\rm dc}$ = 0) for film A.

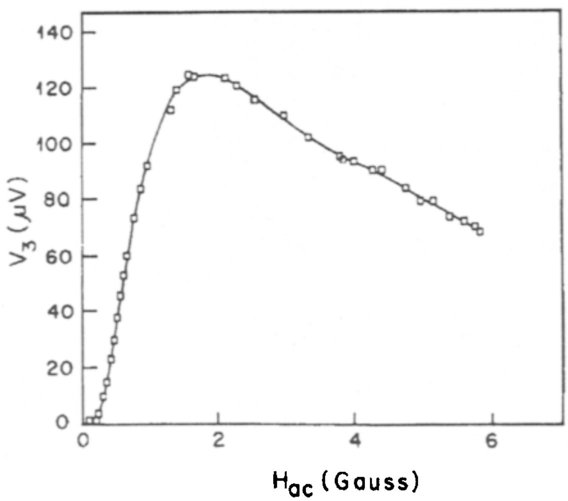


**Figure 5.** Variation of $V_3$ with $H_{\rm ac}$ [$f_{\rm ac}$ = 10 kHz] at 77K for film B.

harmonic starts decreasing when $H_{\rm dc} > 0.7$G. Generalised critical state model [3] indicates that all higher harmonics are expected to decrease monotonically when the applied field ($H_{\rm ac}$+$H_{\rm dc}$) is greater than the full penetration field ($H^*$). For film A, $J_c$ is higher so the full penetration of field occurs at higher value as compared to that in film B. We observe no modulation in the amplitudes of harmonics as observed in bulk superconductor [3], however, in film A, modulation is observed for $V_6$ only in the region where the applied field ($H_{\rm ac}$+$H_{\rm dc}$) is less than full penetration field ($H^*$).

Figure 8 shows the variation of amplitude of third harmonic ($V_3$) with temperature for film B for different value of $H_{\rm ac}$ (0.16G, 0.27G, 0.32G, 0.43G), keeping $f_{\rm ac}$ constant.

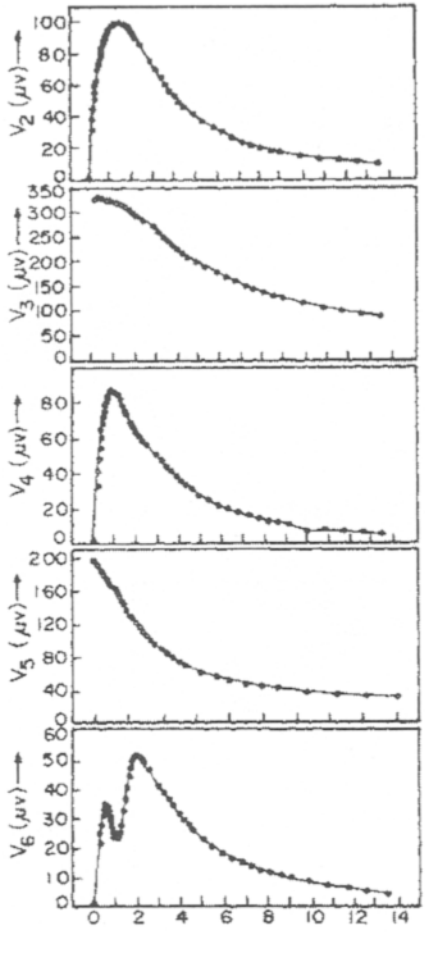


**Figure 6.** Variation of amplitude of harmonics $V_2, V_3, V_4, V_5$ and $V_6$ for film A with $H_{dc}$ [$H_{ac}$ = 4.3G, $f_{ac}$ = 10 kHz, T = 77 K].

$V_3 - T$ curve shows a peak and the amplitude of the peak increases with increase in $H_{ac}$. The third harmonic will appear only when flux starts penetrating into the film, and the magnitude of $V_3$ will increase as more and more flux penetrates. With the increase in temperature, the $J_c$ of the film and hence the $H_{c1}$ will decrease so the penetration of flux in the film will increase. Thus, $V_3$ starts growing and attains a maximum value at the temperature at which the applied flux fully penetrates the film. $V_3$ also depends on the pinning potential at the grain boundaries and near $T_c$ its value decreases very rapidly causing $V_3$ to decrease to zero. Since $V_3$ depends upon the flux penetrating into the film so its value is expected to increase with increase in $H_{ac}$ as observed experimentally. For higher $H_{ac}$, full flux penetration occurs at lower temperature. So the peak in $V_3 - T$ curve is expected to shift to lower temperature with the increase in $H_{ac}$. Figure 9 shows the variation of

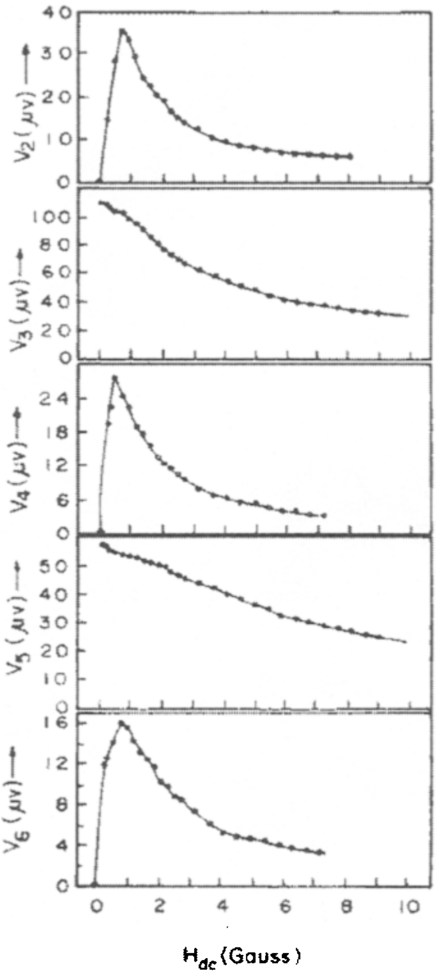


**Figure 7.** Variation of amplitude of harmonics $V_2, V_3, V_4, V_5$ and $V_6$ for film B with $H_{dc}$ [$H_{ac}$ = 1.7G, $f_{ac}$ = 10 kHz, T = 77K].

amplitude of third harmonic ($V_3$) with temperature at different frequency of an ac field for film $B$. As the frequency of ac field is increased, while keeping $H_{ac}$ fixed, the peak in $V_3 - T$ curve shifts towards higher temperature. At higher frequency of ac field, the depth of flux penetration decreases. So, the temperature at which full penetration occurs shifts towards higher side.

Figure 10 shows the variation of $V_3$ with temperature at $H_{ac}$ = 1.5G, $H_{dc}$ = 0 and $f_{ac}$ = 10 kHz for film $B$. $V_3 - T$ curve shows change in slope at 84K which is due to presence of two phases in the Bi(Pb)SrCaCuO high $T_c$ film. It is well known that Bi(Pb)SrCaCuO exists in three phases with nominal compositions 2201, 2212 and 2223 having $T_c$ of 10, 85 and 110 K respectively. XRD pattern of thick films shows the presence of the 2223 high $T_c$ and 2212 low $T_c$ phases. $R - T$ curve of the Bi(Pb)SrCaCuO film is unable to show the presence of 2212 low-$T_c$ phase as percolation path corresponding to high $T_c$ phase is available for the current. However, $V_3 - T$ curve shows clearly the presence of 2212 phase also. For a YBaCuO film consisting of only one phase no such change in slope has been observed [9].

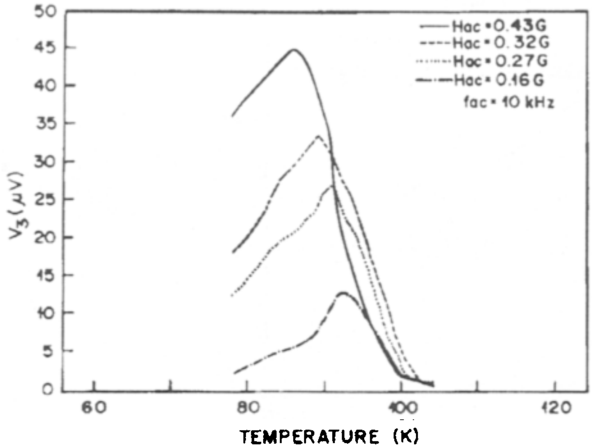


**Figure 8.** Variation of $V_3$ with temperature at different applied ac fields for film B. [$f_{ac}$ = 10 kHz].

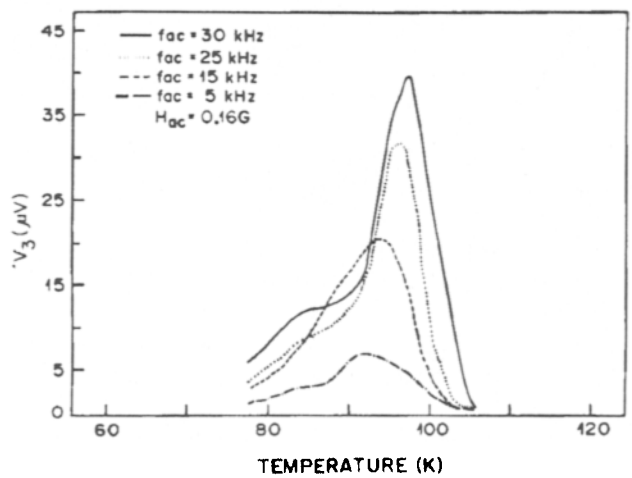


**Figure 9.** Variation of $V_3$ with temperature at different frequencies of ac field for film B. [$H_{ac}$ = 0.16G].

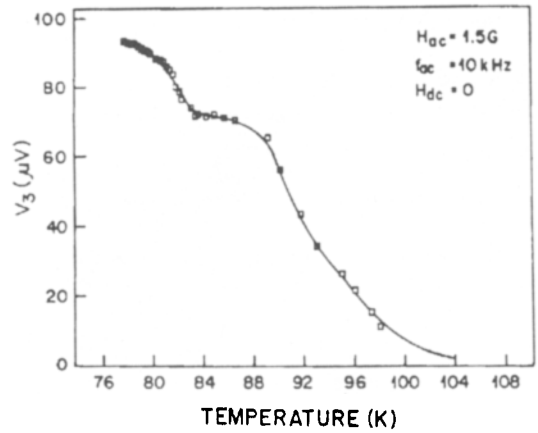


**Figure 10.** Variation of $V_3$ with temperature for film B [$H_{ac}$ = 1.5G, $H_{dc}$ = 0 and $f_{ac}$ = 10 kHz].

## 4. Conclusions

The application of ac field on Bi(Pb)SrCaCuO thick film sample causes generation of odd harmonics. The amplitude of the third harmonic depends on the $J_c$ of the sample. When dc field is applied in addition to ac field, even harmonics are generated. For a small increase in dc field, the amplitude of even harmonics increases whereas amplitude of odd harmonics decreases. The variation of amplitude of third harmonics with temperature confirms the multiphase nature of the sample. $V_3 - T$ curve shows a peak below transition temperature and the peak shifts towards lower temperature with the increase in ac field and towards higher temperature with increase in frequency of ac field.

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## References

[1] N Khare, A K Gupta and G B Donaldson, in *Studies of high temperature superconductors* edited by A V Narlikar (Nova Sci. Publishers, NY 1995) Vol. 14, p.421
[2] C P Bean, *Rev. Mod. Phys.* **36**, 31 (1964)
[3] L Ji, R H Sohn, G C Spalding, C J Lobb and M Tinkham, *Phys. Rev.* **B40**, 10936 (1989)
[4] K H Muller, J C Macfarlane and R Driver, *Physica* **C158**, 366 (1989)
[5] Y B Kim, C F Hempstead and A R Strnad, *Phys. Rev.* **129**, 528 (1963)
P W Anderson and Y B Kim, *Rev. Mod. Phys.* **36**, 39 (1964)
[6] S B Roy, S Kumar, A K Pradhan, P Chaddah, R Prasad, N C Soni and K Adhikari, *Supercond. Sci. Technol.* **8**, 155 (1995)

[7] K Yamamoto, H Mazaki, Yasnoka, K Hirata, T Terasima, K Iijima and Y Bando, *Jpn. J. Appl. Phys.* **28**, 1568 (1989)
[8] A Shaulov, R Bhargava and S Shatz, *J. Appl. Phys.* **69**, 6738 (1991)
[9] N Khare, J R Buckley, R M Bowman, G B Donaldson and C M Pegrum, *Pramana - J. Phys.* **46**, 283 (1996)
[10] S Revenaz, N J Appleyard, T J Jackson and S B Palmer, *Super Cond. Sci. Technol.* **8**, 279 (1995)
[11] N Khare, A K Gupta, S K Srivastava, S Khare and V P N Padmanabhan, *Meas. Sci. Technol.* **8**, 29 (1997)
[12] V P N Padmanabhan and A K Gupta (to be published in *Indian J. Cryogenics*)
[13] J Karthikeyan, A S Paithankar, R Prasad and N C Soni, *Supercond. Sci. Technol.* **7**, 949 (1994)