ac MH loop measurements on Mn doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ superconductors

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Abstract. Isothermal ac MH (magnetization-field) loops for varying field amplitudes were recorded at 77 K on $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-d}$ with $x = 0, 0.010, 0.015, 0.020, 0.025, 0.035$ and 0.050 , $\text{YBa}_2(\text{Cu}_{0.075}\text{Fe}_{0.025})_3\text{O}_{7-d}$, $\text{YBa}_2(\text{Cu}_{0.075}\text{Ni}_{0.025})_3\text{O}_{7-d}$ and $\text{YBa}_2(\text{Cu}_{0.075}\text{Zn}_{0.025})_3\text{O}_{7-d}$ samples up to a maximum field amplitude of 80 Oe. Flat band susceptibility, ac losses and flux profiles were deduced from the ac MH loops. The undoped sample exhibited a minimum weak link ac loss and the 5.0% doped sample showed maximum weak link ac loss. Ni and Fe doped samples showed higher granular losses. J_{cg} estimated from the flux profiles decreases monotonically with increasing concentrations of Mn up to 2.5%.

Keywords. Superconductors; magnetic measurements.

1. Introduction

As the ceramic superconductors are of highly granular nature, the effective usefulness of these materials is determined by the properties of the weak links and the grains together. ac measurements have been useful in studying the weak link behaviour at low field. In ac magnetic property measurements, temperature and field variations of susceptibility are commonly studied while the ac magnetization studies are rare. However, since ac MH loop measurement comprises of the harmonic components, this method is a versatile technique in studying the granular properties. Besides, magnetization measurement can give additional information such as penetration depth, lower critical field, ac losses, etc.

In literature, ac MH loop is reported to have been recorded using electronic integrator method (Fietz 1965; Grover *et al* 1988; Edmond and Firth 1992), analog to digital converter method (Maury *et al* 1990), by summing up of the individually measured harmonic components (Navarro *et al* 1990) etc. $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ is the widely studied system using the MH loop technique. The MH loop obtained has been analysed using exponential model (Grover *et al* 1988) and Kim's model (Edmond and Firth 1992). Ghatak *et al* (1992) studied the harmonic behaviour from the MH loop on the pure and silver doped YBCO samples. Ji *et al* (1997) reported varied shapes of the MH curve for different excitation frequencies and have found that curves obtained at higher frequencies are closer to the one obtained from critical state calculations.

Any defect, grain boundaries, etc in a superconductor act as pinning centres which trap flux and give rise to flux gradient over which screening current flows. This can be further explored by doping. Zheng *et al* (1994) studied the Co and Zn doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ and reported increase in anisotropy on doping. Jirsa *et al* (1998) calculated the penetration depth from the irreversible magnetization region on Mg doped $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ granular samples. Detailed study on ac magnetic hysteresis properties of Mn in $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ is absent in the literature because of the low solubility limit (Jardim and Gama 1989). From the neutron diffraction experiments it is known that Mn occupies Cu(I) site (Saini *et al* 1992a). Dhingra *et al* (1994) reported reduction in diamagnetic signal and broadening of transition beyond 1% Mn doping. Saini *et al* (1992b) also reported reduction in superconducting fraction and broadening of transition. The study on the seebeck coefficient, ac susceptibility and dc magnetic properties on the material had been reported earlier (Isaac Samuel *et al* 1999, 2001; Isaac Samuel and Seshu Bai 2003). In this paper we report the ac magnetization properties of Mn doped YBCO within the low solubility regime through ac susceptibility measurements and have compared it with a Cu(I) site dopant—Fe and two Cu(II) site dopants—Ni and Zn.

2. Experimental

$\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-d}$ samples with $x = 0, 0.010, 0.015, 0.020, 0.025, 0.035$ and 0.050 and $\text{YBa}_2(\text{Cu}_{0.075}\text{Fe}_{0.025})_3\text{O}_{7-d}$, $\text{YBa}_2(\text{Cu}_{0.075}\text{Ni}_{0.025})_3\text{O}_{7-d}$ and $\text{YBa}_2(\text{Cu}_{0.075}\text{Zn}_{0.025})_3\text{O}_{7-d}$ samples were prepared through solid state reaction. The stoichiometric mixture was mixed thoroughly and fired at

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900°C for ~12 h. Mixing and presintering at 900°C was repeated thrice, for homogeneity. Thus prepared presintered powders were pressed into square pellet of size $1 \times 1 \times 0.5$ cm at an uniaxial pressure of ~6T sintered at 930°C for 36 h and furnace cooled. Oxygen annealing was carried out at 450°C for ~60 h. Thus prepared samples were characterized through X-ray diffraction, temperature variation of resistivity and ac susceptibility for phase purity and superconducting properties. XRD pattern revealed that the samples doped with 0–2.5% concentrations of Mn, 2.5% of Fe, 2.5% of Ni and 2.5% of Zn were free from secondary phases, whereas samples with 3.5% and 5% of Mn showed impurity lines of intensity <5% corresponding to $\text{Ba}_3\text{Mn}_2\text{O}_8$ phase. ac MH loops were recorded by integrating the output signal from the secondary coil of a mutual inductance bridge using a phase sensitive detector (PSD) (Gomory 1991; Harish Kumar and Seshu Bai 1996).

3. Results and discussion

Figure 1 shows the magnetization curve at the highest applied field of 80 Oe for the $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-d}$ samples with $x = 0, 0.01, 0.015, 0.020, 0.025, 0.035$ and 0.050 , $\text{YBa}_2(\text{Cu}_{0.075}\text{Fe}_{0.025})_3\text{O}_{7-d}$, $\text{YBa}_2(\text{Cu}_{0.075}\text{Ni}_{0.025})_3\text{O}_{7-d}$ and $\text{YBa}_2(\text{Cu}_{0.075}\text{Zn}_{0.025})_3\text{O}_{7-d}$ samples. The slope of the MH loop indicates the decreasing superconducting volume fraction with doping. Figures 2a–c show the typical field variation of MH loops for the $\text{YBa}_2(\text{Cu}_{0.075}\text{Mn}_{0.025})_3\text{O}_{7-d}$ sample. At very low fields, in perfect diamagnetically shielded state, the MH loop is a reversible straight line with a slope of magnitude equal to the superconducting volume fraction at that temperature and field. At 77 K, except for the pure sample, the slope of the loop was <1

Figure 1. ac Magnetization curve for the $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-d}$ samples with $x = 0, 0.01, 0.015, 0.020, 0.025, 0.035$ and 0.050 , $\text{YBa}_2(\text{Cu}_{0.075}\text{Fe}_{0.025})_3\text{O}_{7-d}$, $\text{YBa}_2(\text{Cu}_{0.075}\text{Ni}_{0.025})_3\text{O}_{7-d}$ and $\text{YBa}_2(\text{Cu}_{0.075}\text{Zn}_{0.025})_3\text{O}_{7-d}$ samples at 80 Oe.

indicating that the entire bulk of the sample is not superconducting. As the field is increased above lower critical field of the weak link (H_{c1w}), flux penetrates into the weak link regions of the sample and exhibits opening up of the MH loop. However, in the present study, even at

Figure 2. ac Magnetization curve for the $\text{YBa}_2(\text{Cu}_{0.075}\text{Mn}_{0.025})_3\text{O}_{7-d}$ sample showing the different characteristic field regions. (a) Initial loop opening—flux entry into weak link region, (b) loop collapse—narrowing of the tail region beyond the weak link full penetration and (c) loop reopening—flux entry into the grains.

minimum applied field of 0.2 Oe, at 77 K, all the samples except the pure one showed opened loop, indicating the lower critical field of the weak links, H_{c1w} , to be < 0.2 Oe. The pure sample shows opening up of loop at ~ 0.7 Oe. After the opening up of loop above H_{c1w} , as more flux penetrates into the weak link region, the loop area increases till the flux reaches the centre of weak link region. This field, at which the flux just reaches the centre of the weak link, is represented as weak link–full penetration field, H_{pw} . Beyond this field, since the superconducting volume fraction of the weak link region reduces, the MH loop collapses and is reflected as an inflexion in the rate at which the loop area increases with the field (figure 3). However, since the upper critical field of the weak links, H_{c2w} , is higher than the lower critical field of the grains, H_{c1g} , the loop does not collapse completely to make a reversible straight line. But the edges of the loop collapse with the opened central region. The slope of the MH loop when the area of the loop has reached the minimum will be < -1 , showing a reduced diamagnetism. This reduced slope corresponds to the diamagnetic grain fraction, f_g . On further increase of field amplitude, the loop once again starts opening up with increasing rate of increase in loop area. This corresponds to the flux penetration into the grains. The field corresponding to the change in rate of increase of loop area with field is taken as lower critical field of the grains, H_{c1g} . Table 1 gives H_{pw} and H_{c1g} for all the samples studied, obtained from the plot of field variation of loop area (figure 3).

3.1 Flat band susceptibility

The ac MH loop recorded is sum resultant of the harmonic components of susceptibility and hence the flat band sus-

ceptibility can be obtained from the MH loops recorded at different field amplitudes. The real (c') and imaginary (c'') components of flat band susceptibility are deduced from the slope and remnant value of the ac MH loop, respectively. The slope is calculated as the ratio of peak magnetization value, M_p , at the peak applied field, H_m , to the peak applied field (i.e. slope = M_p/H_m). The imaginary part of flat band susceptibility is given as (M_{rem}/H_m), where M_{rem} is the remnant magnetization, i.e. the magnetization at zero field amplitude. Figure 4 shows the real (c') and imaginary (c'') components of flat band susceptibility for the $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-d}$ samples with $x = 0, 0.010, 0.015, 0.020, 0.025, 0.035$ and 0.050 , $\text{YBa}_2(\text{Cu}_{0.075}\text{Fe}_{0.025})_3\text{O}_{7-d}$, $\text{YBa}_2(\text{Cu}_{0.075}\text{Ni}_{0.025})_3\text{O}_{7-d}$ and $\text{YBa}_2(\text{Cu}_{0.075}\text{Zn}_{0.025})_3\text{O}_{7-d}$ samples, at 77 K. Since the fundamental harmonic susceptibility is the dominant component of the flat band susceptibility, it can be seen in the figure that the shape of the fundamental harmonic susceptibility is imposed on the flat band susceptibility as well. The real part of flat band susceptibility represents the typical diamagnetic transition of the weak link region with field. As field is increased the diamagnetic signal reduces gradually from a maximum value to a lower value and saturates. The maximum diamagnetic value obtained was -1 for the pure and 1.5% Mn doped sample, while it was < -1 for other sample decreasing with increasing dopant concentration. The volume susceptibility at the saturation region corresponds to superconducting grain fraction (f_g). The superconducting grain fraction, f_g , decreases with increasing dopant concentration. Beyond the saturation region as the field is increased, a further rise in the diamagnetic value of the flat band susceptibility is observed. This corresponds to the flux entry into the grains. The diamagnetic signal from the Zn doped sample was remarkably low, because of its low transition temperature.

Figure 3. Plots of field variation of loop area for the $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-d}$ samples with $x = 0, 0.01, 0.015, 0.020, 0.025, 0.035$ and 0.050 , $\text{YBa}_2(\text{Cu}_{0.075}\text{Fe}_{0.025})_3\text{O}_{7-d}$, $\text{YBa}_2(\text{Cu}_{0.075}\text{Ni}_{0.025})_3\text{O}_{7-d}$ and $\text{YBa}_2(\text{Cu}_{0.075}\text{Zn}_{0.025})_3\text{O}_{7-d}$ samples.

Figure 4. Plots of field variation of flat band susceptibility for the $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-d}$ samples with $x = 0, 0.01, 0.015, 0.020, 0.025, 0.035$ and 0.050 , $\text{YBa}_2(\text{Cu}_{0.075}\text{Fe}_{0.025})_3\text{O}_{7-d}$, $\text{YBa}_2(\text{Cu}_{0.075}\text{Ni}_{0.025})_3\text{O}_{7-d}$ and $\text{YBa}_2(\text{Cu}_{0.075}\text{Zn}_{0.025})_3\text{O}_{7-d}$ samples derived from the ac MH loop at 77 K.

Table 1. H_{pw} , weak link full penetration field, H_{c1g} measured from the field variation of ac susceptibility and that calculated from the flux profile plots and J_{cg} calculated using (2).

Sample	H_{pw} (Oe)	H_{c1g} calculated from $c(H)$ (Oe)	H_{c1g} calculated from flux profile (Oe)	J_{cg} at 77 K ($\times 10^4$) (amp/cm ²)
Mn				
0.0	5.1	41.10	43.85	22.23
1.0	1.5	30.60	35.78	6.05
1.5	7.0	33.50	32.09	3.57
2.0	4.4	28.30	31.06	4.90
2.5	2.8	23.99	27.70	2.62
3.5	2.9	32.57	29.60	7.34
5.0	1.8	27.47	28.35	6.41
Fe				
2.5	2.1	11.60	8.13	1.27
Ni				
2.5	2.7	17.26	18.66	1.74
Zn				
2.5	0.8	17.02	20.89	1.32

The imaginary part of the flat band susceptibility showed a loss peak at the weak link full penetration field, H_{pw} , where the flux just reaches the centre of the weak links. All samples had $H_{pw} < 7$ Oe. This could have been due to the higher porosity and poor coupling between the superconducting grains. The 1.5% Mn doped sample showed the highest H_{pw} of ~ 7 Oe, which reflects the better weak link characteristic observed at 1.5% of Mn doping. Beyond the weak link loss peak, as field is increased above H_{c1g} , the imaginary part of the flat band susceptibility shows a little rise due to the granular losses arising from the flux entry into the grains.

3.2 ac Losses

The area enclosed by the MH loop gives the ac loss per cycle per unit volume and is related to the imaginary part of the fundamental ac susceptibility as (Goldfarb *et al* 1991)

$$c'' = \frac{2m}{H_m^2} \oint M.dH. \quad (1)$$

The area enclosed by the MH loop for the $YBa_2(Cu_{1-x}Mn_x)_3O_{7-d}$ samples with $x = 0, 0.5, 1.0, 1.5, 2.0, 2.5, 3.5$ and 5.0 , $YBa_2(Cu_{0.075}Fe_{0.025})_3O_{7-d}$, $YBa_2(Cu_{0.075}Ni_{0.025})_3O_{7-d}$ and $YBa_2(Cu_{0.075}Zn_{0.025})_3O_{7-d}$ samples, at 77 K, for an applied field of 0.2–80 Oe is shown in figure 3. Typically the log–log plot of the area plotted against the applied field amplitude (H_m) exhibited two different slopes at lower and higher fields with a changeover region in between. The area enclosed by the MH loop at the lower field regime corresponds to the ac losses due to the weak link region and the area at the higher fields corresponds to the granular ac losses. Both the regions showed power relation with the applied field amplitude with an average exponent of 2.63 and 2.96, respectively. In the weak link loss region, i.e. at lower fields, pure sample showed minimum loss and the

5.0% doped sample showed maximum loss. Whereas in the granular loss region, i.e. at high fields, 1.5% sample showed the highest loss. Ni and Fe doped samples also showed higher granular losses. However, Zn showed the least loss. This could be because of the lower superconducting fraction of this sample at that experimental temperature of 77 K.

3.3 Flux profiles

The flux profile within the sample can be obtained from the peak magnetization value (M_p). The normalized penetration is given as (Harish Kumar and Seshu Bai 1996)

$$\frac{p}{R} = 1 - \sqrt{\frac{dM}{dH}}, \quad (2)$$

where p is the radius the flux has penetrated, R the radius of the sample. Figure 5 shows the flux profiles for the $YBa_2(Cu_{1-x}Mn_x)_3O_{7-d}$ with $x = 0, 0.010, 0.015, 0.020, 0.025, 0.035$ and 0.050 , $YBa_2(Cu_{0.075}Fe_{0.025})_3O_{7-d}$, $YBa_2(Cu_{0.075}Ni_{0.025})_3O_{7-d}$ and $YBa_2(Cu_{0.075}Zn_{0.025})_3O_{7-d}$ samples, at 77 K. The flux profile typically increases monotonically to a maximum value at weak link full penetration field, H_{pw} . From this maximum penetration value drops to a lower value as field is increased and remains constant. This region where the penetration remains constant, if extrapolated to zero field, will intercept x-axis at (p^*/R) . From this (p^*/R) superconducting grain fraction, f_{g77} , at 77 K can be estimated as (Ah Dang *et al* 1995),

$$f_g = (1 - (p^*/R))^2. \quad (3)$$

The f_{g77} values obtained using the above relation agrees well with the values obtained from the flat band susceptibility and 77 K field variation of ac susceptibility. As the field is increased, the flux entry into the grains is seen as

Figure 5. Flux profile plots deduced from the ac MH loop for the $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-d}$ samples with $x = 0, 0.01, 0.015, 0.020, 0.025, 0.035$ and 0.050 , $\text{YBa}_2(\text{Cu}_{0.075}\text{Fe}_{0.025})_3\text{O}_{7-d}$, $\text{YBa}_2(\text{Cu}_{0.075}\text{Ni}_{0.025})_3\text{O}_{7-d}$ and $\text{YBa}_2(\text{Cu}_{0.075}\text{Zn}_{0.025})_3\text{O}_{7-d}$ samples.

increase in p/R beyond the (p^*/R) in the flux profile. The field at which p/R starts increasing beyond the constant region is the lower critical field of the grains, H_{c1g} . The estimated H_{c1g} are tabulated in table 1. From the slope, the $dH_m/d(p/R)$ above the H_{c1g} , critical current density of the grains can be estimated as (Ah Dang *et al* 1995),

$$J_{cg} = (dH_m/dp)_{(p=p^*)} \left(\frac{R}{R_g} \right) (1 - (p^*/R)). \quad (4)$$

The J_{cg} estimated using the above relation are tabulated in table 1. The order of magnitude of J_{cg} as well as the trend of variation in J_{cg} values agree well with those calculated from the M_{rem} of the dc magnetization measurements, except for the pure sample for which a higher value is obtained in the flux profile method. This supports the versatility of the flux profile calculations from the MH loops.

4. Conclusions

Isothermal ac MH loops for varying field amplitudes up to a maximum field amplitude of 80 Oe were recorded at 77 K on $\text{YBa}_2(\text{Cu}_{1-x}\text{Mn}_x)_3\text{O}_{7-d}$ samples with $x = 0, 0.010, 0.015, 0.020, 0.025, 0.035$ and 0.050 , $\text{YBa}_2(\text{Cu}_{0.075}\text{Fe}_{0.025})_3\text{O}_{7-d}$ and $\text{YBa}_2(\text{Cu}_{0.075}\text{Ni}_{0.025})_3\text{O}_{7-d}$ samples. From the ac MH loops, flat band susceptibility, ac losses and flux profiles

were deduced. At the minimum applied field of 0.2 Oe, at 77 K, all the samples except the pure one showed opened loop, indicating the lower critical field of the weak links, H_{c1w} , to be < 0.2 Oe. The H_{c1w} for the pure sample was ~ 0.7 Oe. The 1.5% Mn doped sample showed the highest weak link full penetration field, H_{pw} , indicating the better weak link property exhibited by it. In the weak link loss region, i.e. at lower fields, pure sample showed a minimum loss and the 5.0% doped sample showed maximum loss. Ni and Fe doped samples also showed higher granular losses. J_{cg} estimated from the flux profiles is of the order of that obtained from the dc magnetization measurements and exhibits similar trend of variation of J_{cg} with dopant concentration.

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