Irreversibility Lines for $REBa_2Cu_3O_{7-\delta}$ Crystals

L.S. Roleda

De La Salle University, 2401 Taft Avenue, Manila, Philippines lydia.roleda@dlsu.edu.ph

The irreversibility lines (ILs) for high quality REBa₂Cu₃O_{7- δ} crystals (RE = Y and Nd) were determined from complex magnetic susceptibility measurements. The effect of twins on the crystals was also investigated by comparing the ILs for the $YBa_2Cu_3O_{7-\delta}$ samples with and without twins. The $YBa_2Cu_3O_{7-\delta}$ single crystals were grown through the flux method while the intergrowth $Nd_{1/2}Y_{1/2}Cu_3O_{7-\delta}$ crystals were grown using the melt-textured growth technique. Stoichiometric analysis through XRD and EMPA showed a single phase YBa₂Cu₃O_{7- δ} crystal and a dual phase (Nd/Y)Ba₂Cu₃O_{7- δ} composite crystal. The ILs showed the same power law relation, H_{dc} \propto $(1 - t)^n$ for all samples investigated. The ILs were also found to be dependent on ac field amplitude and frequency. The ILs became steeper and shifted to higher temperatures for increasing ac field frequency. Opposite trends were observed for increasing ac field amplitude. The empirical formula $H_{dc} = k[(1-t)/\ln(f_0/f)]^n$ was obtained that accounted for the simultaneous ac field amplitude and frequency dependence. The characteristic frequency f_0 was interpreted to be some limiting parameter, a finding supported by the nonlinear flux diffusion model. The exponent n was found to be dependent on both ac field and frequency. It was found that detwinning increased the T_p-H_{dc} dependence. In addition, there was a weak frequency dependence of the ILs for the intergrowth (Nd/Y)Ba₂Cu₃O_{7- δ} in contrast to a highly responsive "clean" YBa₂Cu₃O_{7- δ} single crystals. This difference strongly indicates an intrinsic characteristic of high $T_{\rm C}$ superconductors.

1. INTRODUCTION

The irreversibility line is a line in the H-T phase diagram below which the magnetic processes are irreversible and above which the processes are reversible. Historically the irreversibility line was discovered in static magnetization observations made after zero-field cooling and field cooling of a sample (K.H. Müller, M. Takasige and G.J. Bednorz, 1987).

AC susceptibility measurements, on the other hand, have also been known to exhibit this irreversibility behavior. Many susceptibility experiments on IL are performed using the peak temperature T_p of the imaginary part of the complex susceptibility curve, χ'' (A. Hein, T.L. Francavilla, and D.H. Liebenberg, 1991). Since

flux pinning is the cause of the magnetic irreversibility for both ac and dc measurements, ac susceptibility measurements can be used for a series of samples with similar grain structure (size, boundaries, fraction, etc.) as a relatively reliable tool for the investigation of their physical properties associated with IL. Moreover, the irreversibility line is an intrinsic property and in high temperature superconductors it marks the thermodynamic boundary between the vortex liquid and the vortex solid based on the notion of vortex melting (R.B. Flippen, 1991).

2. METHODOLOGY

2.1. Sample Preparation

The high purity YBa₂Cu₃O_{7- δ} (or YBCO or Y123) single crystals were flux grown. The mixture was prepared from Y₂O₃, BaCO₃, and CuO powders that were thoroughly mixed using a rotating mixer and packed tightly into a TiO₂ stabilized Y₂O₃ crucible. The crucible was then placed in a furnace. The heating cycle is shown in Fig. 1. The crystals grown had well-defined *a*-*b* sides as evident in Fig. 2. These crystals were later oxygenated in order to enhance their superconducting transition temperature *T*_C. Oxygenation, however, led to the formation of twins in the crystals.

Polycrystalline $(Nd/Y)Ba_2Cu_3O_{7-\delta}$ (or [Nd/Y]BCO or [Nd/Y]123) was prepared using the conventional solid-state reaction method. A stoichiometric powder mixture of the pure compounds Nd₂O3, Y2O3, BaCO3 and CuO was sintered at 900°C for 24 hours, then ground to form feedstock. The feedstock was then hand pressed into rectangular bars and heated at 940°C for 24 hours. Each bar was cut into a smaller size then suspended in air in a vertical furnace by nichrome wire attached to a zirconia insulator passing through the top of the bar. The bar was then subjected to the heating cycle shown in Fig. 3. Samples were cleaved from the very large crystal domains that resulted. Figure 4 shows a melt-textured growth bar cleaved into several pieces. Although the $(Nd/Y)Ba_2Cu_3O_{7-\delta}$ crystals could not be easily seen from the figure, these could be obtained by cleavage and the sides polished to remove excess flux. A large, shiny, black (Nd/Y)Ba₂Cu₃O_{7-δ} is shown in Fig. 5. The bar was annealed in 1 atm of pure oxygen at a temperature of 475°C for 24 hours, followed by a slow cooling process at 1°C/h on oxygen to 150°C and then quenched to room temperature.

2.2. Characterization

The samples were initially characterized using the X-ray diffraction and electron microprobe analysis. The XRD patterns were record-

ed by a computer controlled Siemens powder diffractometer with a Cu target. A nickel filter was used to reduce the CuKB component leaving a monochromatic $CuK\alpha_1$ radiation (λ = 1.540562Å). Angular scans from $2\theta = 5^{\circ}$ to 2θ = 60° were performed at the rate of 1.0° per minute in steps of 0.01°. The sample was mounted with the *c*-axis normal to the plane of the sample holder to ensure high intensity (001) Bragg reflections. Figures 6 and 7 shows the XRD patterns for YBa₂Cu₃O_{7-δ} and $(Nd/Y)Ba_2Cu_3O_{7-\delta}$ crystals, respectively. It can be seen from Fig. 6 that the $YBa_2Cu_3O_{7-\delta}$ crystal was highly oriented with the (001) peaks dominating the patterns. This indicates that the crystal was of high purity Y123 phase or that there was no trace of unreacted green phase (Y211). On the other hand, the XRD pattern for intergrowth (Nd/Y)Ba₂Cu₃O_{7-δ} crystal is dominated by the 00l peaks indicating that the (Nd/Y)123 phase is the majority phase. The relatively higher 004 peak as compared to that for the $YBa_2Cu_3O_{7-\delta}$ sample implied the presence of the (Nd/Y)211 phase.

The stoichiometry of the YBCO sample was found to be $Y_{1.01}Ba_{1.99}Cu_{3.00}Sr_{0.11}O_{7-\delta}$, indicating that indeed the sample is of high purity and high quality single phase material. As for the intergrowth (Nd/Y)BCO sample, the stoichiometry for the (Nd/Y)123–phase was (Nd/Y)_{0.99}Ba_{1.95}Cu_{3.00}Sr_{0.10}O_{7-\delta} and for the (Nd/Y)211–phase,

 $(Nd/Y)_{1.94}Ba_{0.99}Cu_{1.00}Sr_{0.04}O_{5-\delta}$. It is worth mentioning that the twin patterns for the fluxgrown high purity $YBa_2Cu_3O_{7-\delta}$ and the intergrowth $(Nd/Y)Ba_2Cu_3O_{7-\delta}$ crystals have remarkable resemblance, as shown in Fig. 8.

2.3. Detwinning Process

Twin patterns result from the crystal's transformation from tetragonal to orthorhombic structure. During the transformation of the T–O phase, the *a*–axis contracted while the *b*–axis lengthened. This results to an internal stress. The formation of twins relieves the transformation stress. Detwinning was performed to YBa₂Cu₃O_{7- δ} samples only. A pressure was applied on the two parallel edges of the crystal then heating it in oxygen. A pressure of approximately $10^7 - 10^8$ N/m² was applied across the sides of the sample using a homemade instrument. The crystal was heated to 470°C for three hours in flowing oxygen and then quenched. It was observed that the detwinning procedure worked satisfactorily as the twins disappeared from the crystal but some of them reappeared after reoxygenation. In addition, most twins reappeared near the uneven edge of the crystal. This may be caused by the unbalanced pressure applied to the sides of the crystal due to its irregular shape. Cutting off the portion which contained the most twins was a last recourse. For a consistent investigation on the effect of twins, magnetic susceptibility measurements were made on the same crystal sample before and after detwinning.

2.4. Magnetic Susceptibility Measurements

The magnetic susceptibility apparatus employed the principle of mutual inductance. The real and imaginary components of the magnetic susceptibility as a function of sample temperature, $\chi'(T)$ and $\chi''(T)$, respectively, were measured simultaneously as the in-phase and out-ofphase components in terms of other experimental parameters such as the applied dc magnetic field, H_{dc} , ac field amplitude, h_{ac} , and ac field frequency or the excitation frequency, f. The caxis of the samples was oriented parallel to the field. The dc field was supplied by a copper wound solenoid which could generate fields up to about 2kG. The driver coil ac current provided the ac rms field. The excitation frequency was controlled using the lock-in amplifier. All data (from the lock-in-amplifier and the temperature controller) were recorded and stored in a PC computer linked to the susceptibility system. The peak temperature is the temperature at which the imaginary part of the magnetic susceptibility curve exhibits a peak, as shown in Fig. 9. The peak temperature was determined for each susceptibility run involving a combination of the parameters H_{dc} , h_{ac} , and f.

3. RESULTS AND DISCUSSION

3.1. YBa₂Cu₃O_{7-δ} single crystal with twins

Figure 10 shows the logarithmic plot of the irreversibility lines for high purity, high quality $YBa_2Cu_3O_{7-\delta}$ single crystal with twins. The lines drawn in the figures mentioned from hereon are actual fits to the data. It is noticeable that the position of these lines depended also on $h_{\rm ac}$ and f. The straight lines obtained implies that the $H_{dc}-T_p$ relationship follows a scaling factor of the form $H_{dc} \propto (1-t)^n$, where Tp is expressed in terms of the reduced temperature t ($t = T_p/T_x$, where $T_x = 90.5$ K). The temperature parameter $T_{\rm x}$ was so chosen such that it was the value that yielded the best fit for all the H_{dc} - T_p data. Similar power-law relation was also reported by other authors [4-7]. The exponent *n* is found to be dependent on both the ac field amplitude and the frequency, in agreement with the report of Emmen (Emmen, G. M. Stollman and W. J. De Jonge, 1990). Table 1 shows the different values of n for different ac field amplitudes and driving frequencies.

For a particular driving frequency, such as in Fig. 11, the irreversibility lines tend to shift to lower temperatures for increasing ac field amplitude. This is explained within the framework of the critical state model (G. Blatter, M.V. Feigel'man, V.B. Geshkenbein, A.I. Larkin and V.M. Vinokur, 1994), increasing the magnetic field implies an increase in the Lorentz forces which in turn calls for stronger pinning forces to maintain equilibrium, and hence lower T_p 's. As a result, *n* generally decreases with increasing h_{ac} . In the same manner, the frequency dependence of the IL stems from the fact that the temperature at which the peak in the χ'' curve occurs at higher values for increased driving frequency. Müller (K.H. Müller, 1990) explained that as the frequency is increased, there is less time to penetrate to the center of the sample. To compensate for this less efficient creep, there should be a weaker pinning force. Hence, this would mean a higher temperature for $T_{\rm p}$. Conversely, for decreasing frequency the IL tends to be steeper, as shown in Fig. 12 where the ac field amplitude is 9.13G and *n* ranges from 1.45 for f = 20kHz to 3.94 for f = 1kHz.

Simultaneous ac field amplitude and frequency dependence of the irreversibility line was determined by assuming an expression of the form similar to the above relation. Specifically,

$$H_{dc} = k \left[\frac{1-t}{\ln(f_0/f)} \right]^n \tag{1}$$

where k is some constant associated with h_{ac} and f_0 is a characteristic frequency. Applying this equation to the graphs in Fig. 10 yielded the slope and п the intercept $A = \ln k - n \ln [\ln (f_a/f)]$. As for the determination of k, a plot of $\exp[-A/n]$ vs ln f was constructed for each ac field amplitude where k and f_0 can be obtained from the slope and intercept, respectively. Although h_{ac} is contained in the constant k the explicit dependence of the irreversibility line on h_{ac} cannot be determined here because k is considered an empirical constant. Other factors such as the sample's dimension, its orientation in the field, may also be contained in k. On the other hand, f_0 is approximately 20kHz, 36kHz, and 34kHz for h_{ac} = 9.13G, 4.56G, and 2.28G, respectively. It was observed that, for $h_{ac} = 9.13$ G, no measurement was possible for driving frequencies larger than 20kHz. Also, equation (1) failed to describe the $H_{\rm dc}-T_{\rm p}$ relationship for driving frequency f =45kHz for h_{ac} = 2.28G and 4.56G. Hence, it appears that f_0 is some limiting parameter that is a function of the ac field amplitude. A possible explanation is provided by the nonlinear flux diffusion model [11] which describes the pinning energy U as

$$U \approx G(T) \ln\left(\frac{f_0}{f}\right) \tag{2}$$

where G(T) is some function of temperature. This implies that for frequencies larger than f_0 , $\ln(f_0/f)$ becomes negative and equation (2) is no longer meaningful.

3.2. Detwinned YBa₂Cu₃O_{7-δ} single crystal

The irreversibility lines for detwinned $YBa_2Cu_3O_{7-\delta}$ single crystal were determined under the following experimental conditions: $h_{ac} = 2.28, 4.56, 9.13$ G; f = 0.5, 1, 10, 20kHz. It is noticeable that the ILs also obeyed a power law dependence. That is, $H_{dc} \propto (1 - T_p/T_x)^n$, where the variables were defined in the same fashion as in the preceding section. In addition, the values of *n* were observed to be affected by the ac field amplitude and frequency. This feature can be seen on Table 2. Comparison with Table 1 reveals a weaker n dependence for $YBa_2Cu_3O_{7-\delta}$ crystal after the removal of twins. However, since the peak temperature is investigated as a function of H_{dc} , it can be seen that T_{p} varies with H_{dc} as an inverse of *n*. Hence, it can be deduced that detwinning increases the dependence of the peak temperature on the dc field implying that even small dc fields can produce a considerable change in the temperature at which the peak in χ'' curve occurs. Figure 13 shows a comparison between ILs of the crystal before and after it is detwinned for h_{ac} = 2.28G and f = 10 kHz. It is noticeable that the IL for the sample with twins is steeper than that without twins, the value of n decreased from around 4 to 2.5. This means that the T_p dependence on H_{dc} increased from 0.25 to 0.4 when the twins were removed. The values of T_p also shifted to higher values after the sample was detwinned.

The position of the ILs for detwinned $YBa_2Cu_3O_{7-\delta}$ tended to shift to lower temperatures for increasing ac field amplitude, as shown in Fig. 14. This was a similar behavior observed for the same sample before it was detwinned. However, for frequencies larger than 1kHz, the ILs looked steeper for increasing frequency, and appeared to be independent of the frequency for f = 1kHz and 500Hz, as shown in Fig. 15. For ac field amplitude 2.28 and 4.56G, the frequency dependence was found to take the same logarithmic form as equation (1). The characteristic frequencies were found to be 25kHz and 18kHz for ac field amplitudes of 2.28G and 4.56G, respectively.

Magnetic susceptibility measurements at 45kHz were not possible for both ac fields. This observation is again consistent with the nonlinear flux diffusion model.

On the other hand, with regard to the apparent frequency independence of the irreversibility lines for lower frequencies, similar results were obtained by Flippen (R.B. Flippen, 1991) for his ceramic YBa₂Cu₃O_{7-δ}. He explained that the frequency independence of the results below 1kHz suggests that the flux vortices can move in time with the ac field and thus represent a stable state; above this frequency the vortices cannot move in synchronism with the ac field and a different dynamic state results. The vortex glass picture of superconductivity given by Fisher (M.P.A. Fisher, 1989) predicted this kind of behavior in that as the frequency of the measurement approaches zero, a finite IL results where the χ'' peak temperature now represents a "glass transition" temperature for the vortex system. The glassy phase of a superconductor has the dynamic properties of a highly viscous liquid, wherein the vortices are "locked to a particular state."

3.3. Intergrowth (Nd/Y)Ba₂Cu₃O_{7-δ} crystal

Unlike the YBa₂Cu₃O_{7- δ} single crystal, the intergrowth Nd_{1/2}Y_{1/2}Ba₂Cu₃O_{7-δ} crystal exhibited a substantial shift in the temperature corresponding to the peak in the χ'' curve as the applied dc field was varied for a fixed ac field amplitude and frequency. This sample appeared to be more responsive to H_{dc} , compared to the $YBa_2Cu_3O_{7-\delta}$ samples. On the other hand, like YBCO samples, its irreversibility lines revealed a power law dependence: $H_{dc} \propto (1 - T_p/T_x)^n$, with the temperature parameter $T_x = 94$ K. Similar conditions, as discussed earlier, were imposed in choosing the value of T_x . Figure 16 shows that the position of ILs for various frequencies at ac field amplitude of 0.35G. Although the $T_{\rm p}$'s shifted to larger values for increasing frequency, it was found that the ILs were weakly affected by the frequency of the ac field for frequencies 1, 2, 5, and 10kHz. Except for 5kHz, data fitting resulted in an increasing

applied dc field dependence of the reduced temperature with frequency, a characteristic also exhibited by the Y123 crystal. Figure 17 shows the log-log plot Fig. 16 with the values of n = 1.0, 1.5, 2.5, 2.0, 2.4, and 2.3 for frequencies 45, 20, 10, 5, 2, and 1 kHz, respectively. This implies that the composite (Nd/Y)123crystal demonstrateed a characteristic similar to that for other high T_c cuprate superconductors. Most of the reported ILs (J.A. Xia, H.T.Ren, Y. Zhao, C. Andrikidis, P.R. Munroe, H.K. Liu and S.X. Dou, 1993, A. Nishida and K. Horai, 1990, Y. Yeshurun and A.P. Malozemoff, 1988, K.H. Müller, 1990) showed ILs with almost the same H_{dc} - T_p power law relation with $\frac{1}{2} \le n \le 3$. This is interesting to note since this behavior is not apparent in the high purity, high quality YBa₂Cu₃O_{7-δ} samples which showed quite a variation of n values. This difference in the response of a doped sample and a clean, twin-free sample can be an indicator of an intrinsic property of high $T_{\rm C}$ superconductors.

Furthermore, investigation of the frequency dependence of the irreversibility lines, though weak, showed a logarithmic relation similar to that for the Y123 samples. The characteristic frequency was found to be much larger than 45kHz, the highest measurement frequency. Although this denoted that ac susceptibility measurements for larger frequencies could be performed, it was not pursued because the highest measurement frequency used for Y123, from which data comparison would be made, was only 45kHz.

4. CONCLUSION

The dc field irreversibility lines for YBa₂Cu₃O_{7- δ} single crystal and intergrowth (Nd/Y)Ba₂Cu₃O_{7- δ} crystal were determined for different ac field amplitudes and frequencies. The ILs for these samples showed the same power law relation, particularly, $H_{dc} \propto (1-t)^n$. It was found that the ILs for were dependent on both the ac field amplitude and frequency. An

empirical relation
$$H_{dc} = k \left[\frac{1-t}{\ln(f_0/f)} \right]^n$$
 was

conjectured to account for this simultaneous $h_{\rm ac}$ and f dependence. The removal of twins in the YBa₂Cu₃O_{7- δ} sample resulted in a stronger $T_{\rm p}$ - $H_{\rm dc}$ dependence. In addition, the response of high purity theYBa₂Cu₃O_{7- δ} sample to dc field was found to be different to that of the composite (Nd/Y)Ba₂Cu₃O_{7- δ} sample and other common high $T_{\rm C}$ cuprate superconductors. This difference can be an indicator of an intrinsic property of high $T_{\rm C}$ superconductors.

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Equations:

Eq. 1
$$H_{dc} = k \left[\frac{1-t}{\ln(f_0/f)} \right]^n$$

Eq. 2 $U \approx G(T) \ln\left(\frac{f_0}{f}\right)$

Table 1. Values of <i>n</i> [from $H_{dc} \propto (1-t)^{1}$	ⁿ] at Different Driving Frequencies
and ac Field Amplitudes for Y	/Ba ₂ Cu ₃ O _{7-δ} Single Crystal

	ac field amplitude			
frequency	2.28G	4.56G	9.13G	
40kHz	1.52	1.80		
20kHz	2.80	2.03	1.45	
10kHz	4.45	3.63	2.40	
1kHz	6.26	3.33	3.94	

Table 2. Values of <i>n</i> [from $H_{dc} \propto (1-t)^n$] at Different Driving
Frequencies and ac Field Amplitudes for Detwinned
YBa ₂ Cu ₃ O _{7-δ} Single Crystal

	ac field amplitude		
frequency	2.28G	4.56G	9.13G
20kHz	0.88		1.1
10kHz	2.48	2.59	6.93
1kHz	2.73	5.28	2.71
0.5kHz	2.29	5.53	2.29



Figure 1. Heating Cycle for High Quality, High Purity YBa₂Cu₃O_{7-δ} Single Crystals



Figure 2. A Selection of YBa₂Cu₃O_{7-δ} Single Crystals Grown Using BaO/CaO Flux Method (Background Scale: Each Side is 1mm)



Figure 3. Heating Cycle for (Nd/Y)Ba₂Cu₃O_{7-δ} Crystals



Figure 4. Melt-Textured (Nd/Y)Ba₂Cu₃O_{7-δ} Bar Cleaved into Several Pieces



Figure 5. Cleaved and Polished (Nd/Y)Ba2Cu3O7-δ Crystal



Figure 6. XRD Patterns for YBa₂Cu₃O_{7-δ} Single Crystal



Figure 7. XRD Patterns for (Nd/Y)Ba₂Cu₃O_{7-δ} Crystal



Figure 8. Twin Patterns from Cross Polarized Micrograph of the YBCO (top) and (Nd/Y)BCO (bottom) Crystals. (magnification: 400 times)



Figure 9. χ -T Curves for YBa₂Cu₃O_{7- δ} Crystal (f = 20kHz, h_{ac} = 2.28G) T_p is the Temperature where χ '' Exhibits a Peak.



Figure 10. Logarithmic Plot of the Irreversibility Lines for YBa₂Cu₃O_{7-δ} Crystal at ac Field Amplitudes *top*, 2.28G; *middle*, 4.56G; and *bottom*, 9.13G.



Figure 11. Irreversibility Lines for YBa₂Cu₃O₇₋₈ crystal at Different ac Field Amplitudes and a Driving Frequency of 20kHz







Figure 13. Comparison of the Irreversibility Lines for YBCO Single Crystal Before and After Detwinning. $h_{ac} = 2.28G$, f = 10kHz



Figure 14. Irreversibility Lines for Detwinned YBa₂Cu₃O_{7-δ} Crystal at Different ac Field Amplitudes and Frequency 10 kHz



Figure 15. Irreversibility Lines for Detwinned YBa₂Cu₃O_{7-δ} Crystal Showing Frequency Dependence







Figure 17. Logarithmic Plot of Fig. 16