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Study and Analysis of Zinc Substitution in $YBa_2Cu_3O_7$- Δ

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Abstract

The oxygen isotope effect in Zn doped superconductivity $YBa_2Cu_3O_{7-\delta}$ was investigated. Zn goes into the Cu plane site. The shift in critical temperature (ΔT_C) between samples oxygenated in ^{18}O and ^{16}O was obtained via dc resistance measurements, and low field dc magnetization and ac susceptibility

Introduction

SAMPLE PREPARATION

The stoichiometric proportions for the Zn system $YBa_2(Cu_{1-z}Zn_z)_3O_{7-\delta}$ with z = 0.02, 0.025, 0.04, 0.05, 0.06, 0.07, 0.075, 0.08, 0.085, and 0.0875 were prepared in a different manner than the previous two systems. The calculation procedure was as follows:

1. heat to 925˚C in air and hold for 20 hours, then cool and regrind;
2. repeat step 1;
3. heat to 930˚C in $^{16}O$and hold for 12 hours; then
4. cool to 475˚C and hold for 18 hours; then
5. cool to 375˚C and hold for 12 hours; then
6. cool to room temperature

The sintering process was as follows:

1) heat to 925˚C and hold for 12 hours; then
2) cool to 475˚C and hold for 24 hours; then
3) cool to 375˚C and hold for 18 hours; then
4) cool to room temperature.

All cooling processes were at the natural cooling rate of the oven.

MEASURMENTS

The substitution of Zn for Cu in $YBa_2Cu_3O_{7-\delta}$ causes a more rapid depression in the critical temperature with the increase in Zn concentration than it did with the Pr substitution. The resistivity measurements (Figure 1) show a smooth drop in the critical temperature with the increase of Zn substitution, from about 70K at 2% Zn to just under 10K at 8.75% Zn. A substitution of 9% Zn remained in the normal state down to 1.8K. These measurements also indicate an increase in the normal state resistivity with the drop in T_c and the increase in Zn concentration.

A comparison of the dc magnetization, ac susceptibility and resistivity measurements is given in Figure.2. The 4% Zn substitution is given as a characteristic sample. The Zn system has the sharpest transitions of all three of the systems studied. The transition width remains sharp and independent of the Zn concentration (and critical temperature). There is good agreement between the calculated isotopic shifts as well as the critical temperatures determined from the three different measurement methods. The difference between T_c obtained magnetically and that obtained resistively is highest for the 4% Zn samples. The linear relationship between the critical temperature and the concentration can be seen in Figure 3.

The ZFC and FC data for several Zn concentrations are given in Figure 4, and the Meissner fraction indicated in Table 1. The Meissner are fraction drops rapidly with the initial increase in Zn substitution but then quickly levels out around 10%. At the highest concentrations of Zn, 8%, 8.5% and 8.75%, the Meissner fraction no longer remains small or predictable.

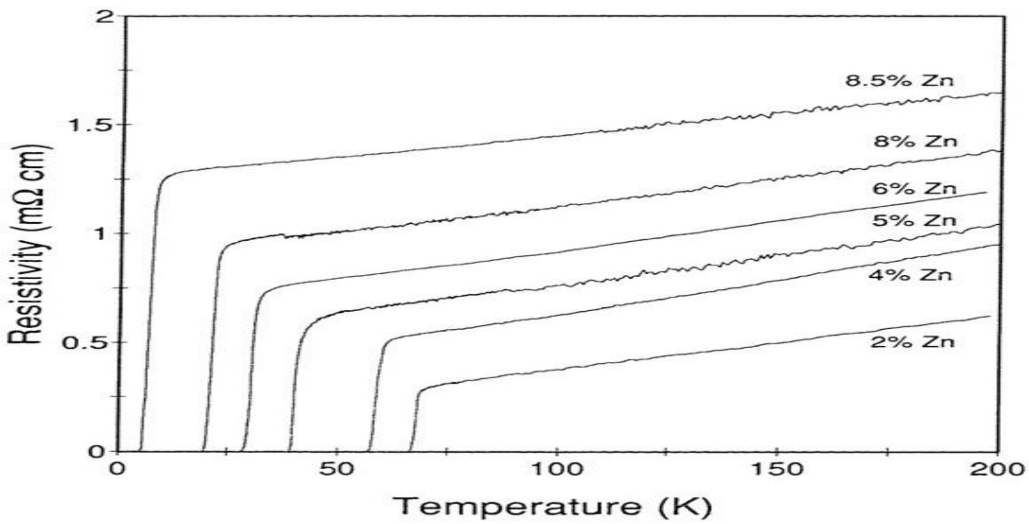

Figure 1

DC resistivity vs. temperature for Zn substituted YBCO. Only the measurements on the some of the $^{16}0$ samples are shown. Note the linear slope of the samples in the normal state.

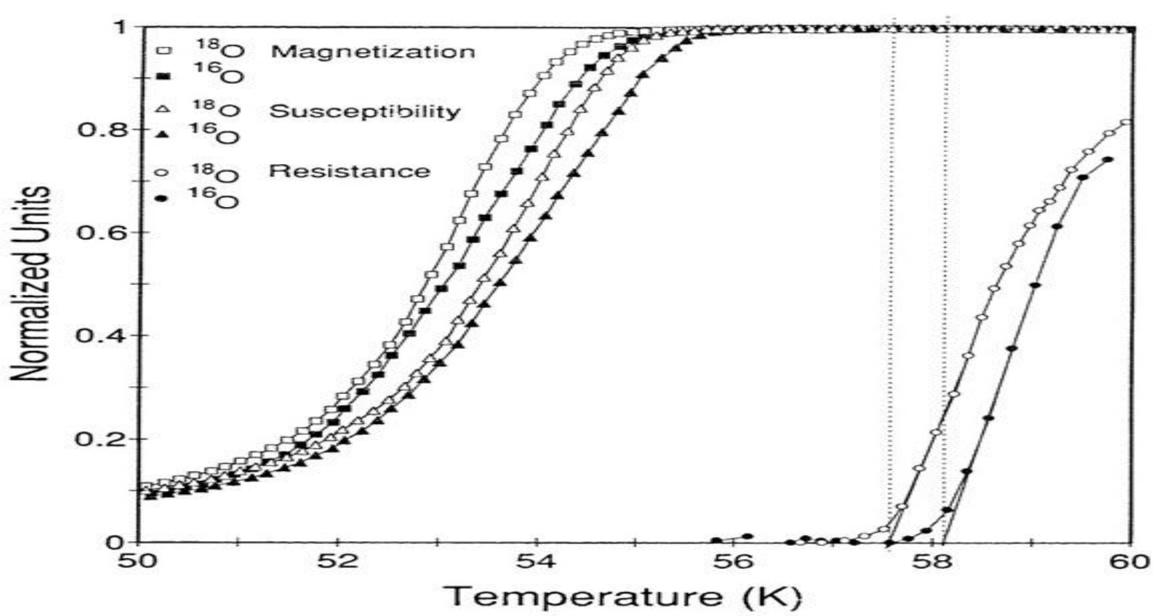

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Figure .2

Comparison of dc magnetization, ac susceptibility and resistance measurements for $YBa_2(Cu_{0.96}Zn_{0.04})_3O_{7-\delta}$. The symbols represent the data. The solid lines provide continuity from point to point. The dashed lines are a visual aid for the critical temperature of theresistive transition (obtained from the straight line approximation). The resistance was normalized to R(72K).

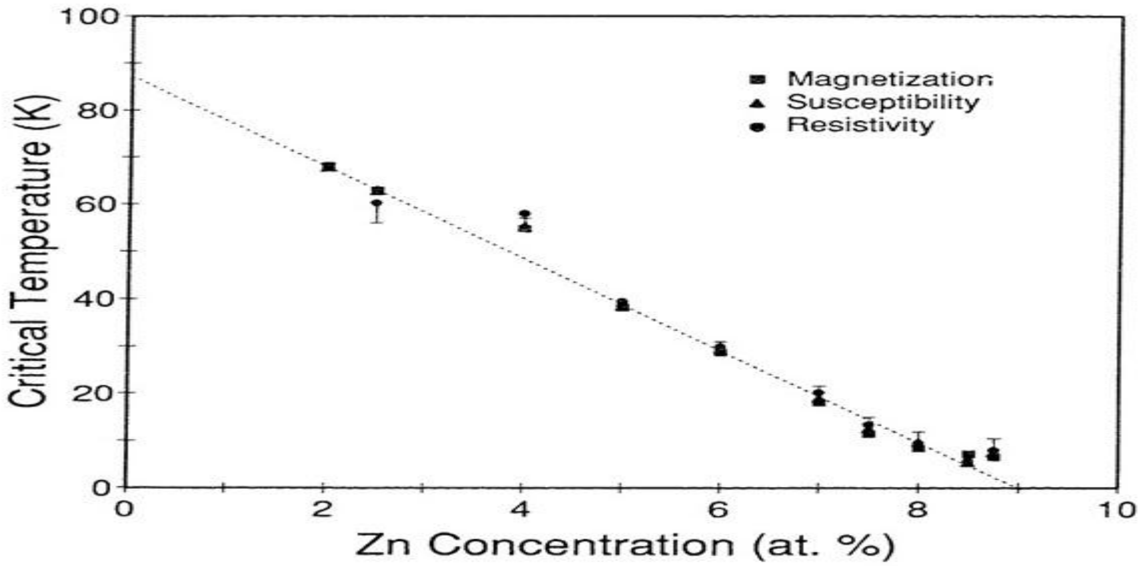

Figure .3 Critical temperature vs. Zn concentration. The dotted line is a linear fit to the data and indicates the linear relationship between the concentration and T_c

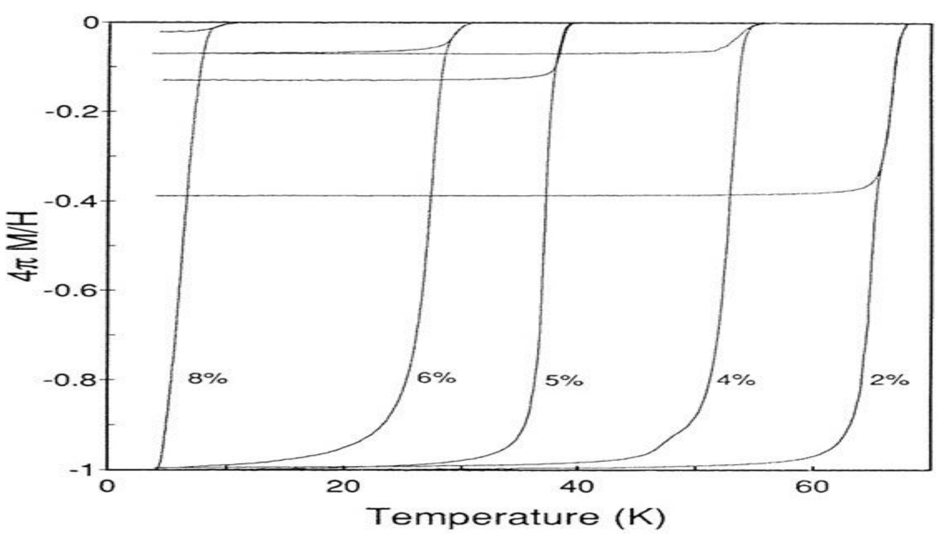

Figure 4

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Meissner effect in Zn substituted YBCO. Both the ZFC and FC curves are shown from which the Meissner fraction has been obtained for the 2%, 4%, 5%, 6%, and 8%Zn samples. Samples were measured in a field of strength 0.05Oe.

Zn concentration	^{18}O concentration	Meissner Fraction	Transition Width (K)		
(at.%)	(at.%)	@0.05Oe	Mag.	Susc.	Res.
2	92	40%	3.5	3.5	1.0
2.5	(92)	60%	22	22	6
4	92	7%	3.9	4.5	1.5
5	92	13%	3.0	2.0	1.3
6	(92)	7%	5.0	3.0	1.6
7	86	6%	4.0	2.5	2.2
7.5	88	5%	3.9	2.6	2.0
8*	(92)	2%,11%	2.9	2.4	2.0
8.5 *	92	74%,60%	2.3	2.2	2.0
8.75 *	92	5%,25%	2.0	2.0	2.0

Table 1 . General character tics of Zn substituted YBCO

* both ^{16}O and ^{18}O Meissner fractions are given. A number in parentless indicates that this value is an estimate Our results on the resistivity, critical temperature, and the generally narrow transitions involved in Zn substitution agree quite favorably with what exists in the literature No information on the Meissner effect is available.The data the simplex fit to the data , and the isotopes for the dc magnetism ,ac susceptibility and resistivity measurement for the Zn substitution of 2% to 8.75% are given in Figure 8.5 to 8.14. The critical temperature and the computed isotope shift are given in Table 8.2 . The isotopic shift ΔT_c ,and the isotope coefficient, α, are plotted against Tc in figure8.15. The isotope shift appears constant or there may even be a slight decrease in its magnitude with decreasing critical temperature. Only the magnetic measurement for the8.5% and 8.75% samples, as well as all measurement on the 8% samples have large ΔT_C 's

The Zn samples do not show (to within the limits of the equipment) any impurity lines within the X-ray spectra; they have sharp transitions; and thus, tend to be better qualify samples than the Pr or Pr:Ca series. The quality of the 2.5% Zn substituted sample is questionable as it has an extremely broad transition, however it does give an isotopic shift that is comparable to the other measured shifts. The 4% anti 7% Zn samples were subjected to different measuring fields ranging from 0.05Oe to 50Oe to study the effect of the penetration of the measuring field into the sample. The effects on the ZFC curves are shown in Figure 8.16.On the low T_C sample, 7% Zn, a measuring field of only 1Oe has already begun to penetrate the sample causing a substantial decrease so signal. Not only is the magnitude of the transition lessened. but indeed the shape of the entire transition is altered. Even samples with high T_C's (4% Zn) can be influenced by their measuring field although this occurs only at lowers fields. There appears to be a critical field at which there is large change in The empty symbols represent the ^{18}O data and the filled symbols represent the ^{16}Odata. The solid line represents the Simplex fit to the data. The "+" symbols represent the shift, ΔT_i, as a function of temperature, between the two fits to the data.

The arrows on the magnetization and susceptibility graphs indicate the T_C obtained from a linear extrapolation of the bulk of the transition – 68.1K for the magnetization (upper limit = 68.7K) and 67.9K (upper limit = 68.9K) for the susceptibility. No cutoff was imposed in the calculation of the mean of the isotope shift for either the magnetic or resistance measurements. A lower limit cutoff was imposed on the resistance owing to the long resistive tails. The cutoff was taken at which the fit broke away from the straight line extrapolation which has extend to 0.7.

The resistance measurements are normalized lo R(80K). Not all temperature scales are equivalent.

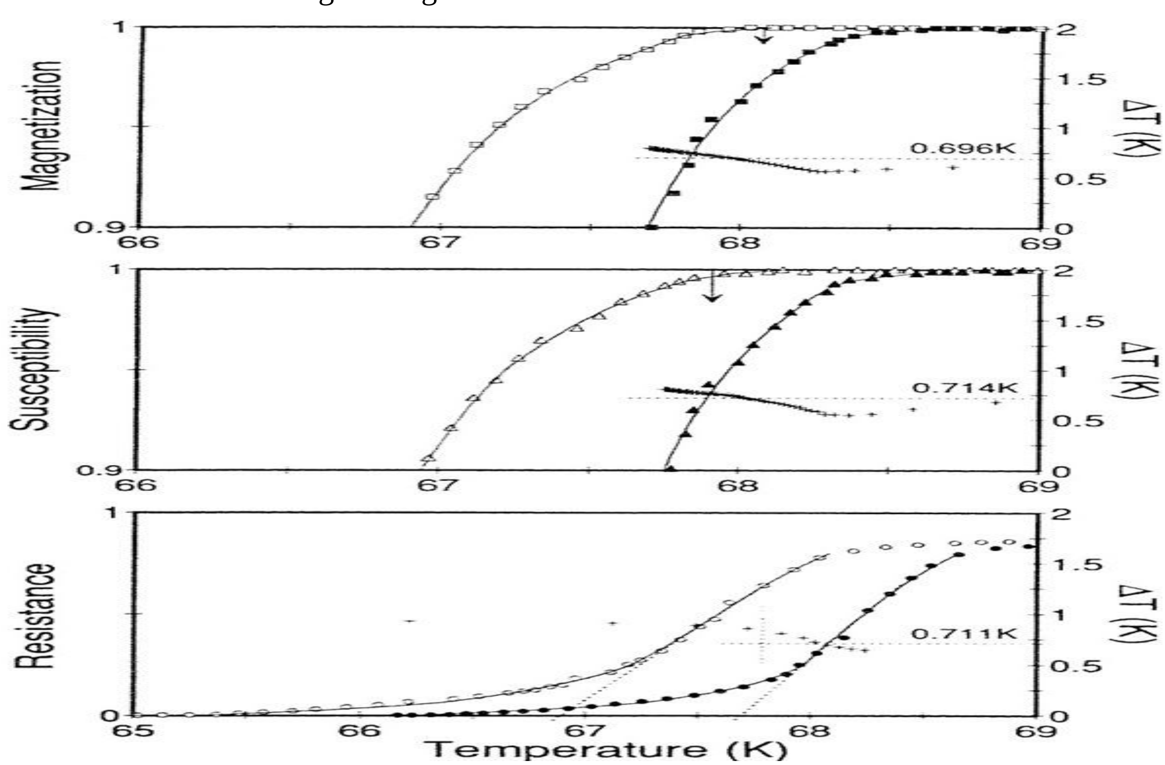

Figure .5 Oxygen isotope effect in $YBa_2(Cu_{0.98}Zn_{0.02})_3O_{7-\delta}$4% Zn Substitution 2.5% Zn Substitution

The empty symbols represent the ^{18}O data and the filled symbols represent the ^{16}Odata. The solid line represents the Simplex fit to the data. The "+" symbols represent the shift, ΔT_i: as a function of temperature, between the two fits to the data. The arrows on the magnetization and susceptibility graphs indicate the Tc obtained from a linear extrapolation of the bulk of the transition – 62.9K for the magnetization (upper limit = 63.4K) and 63.0K (upper limit = 63.7K) for the susceptibility. No cutoff was imposed in the calculation of the mean of the isotope shift for either the magnetic or resistance measurements. Although the resistive transition is quite is poor, the temperature shift, ΔT_i, between curves remains constant and thus no cutoff limit was imposed.

The resistance measurements are normalized lo R(100K). Not all temperature scales are equivalent.

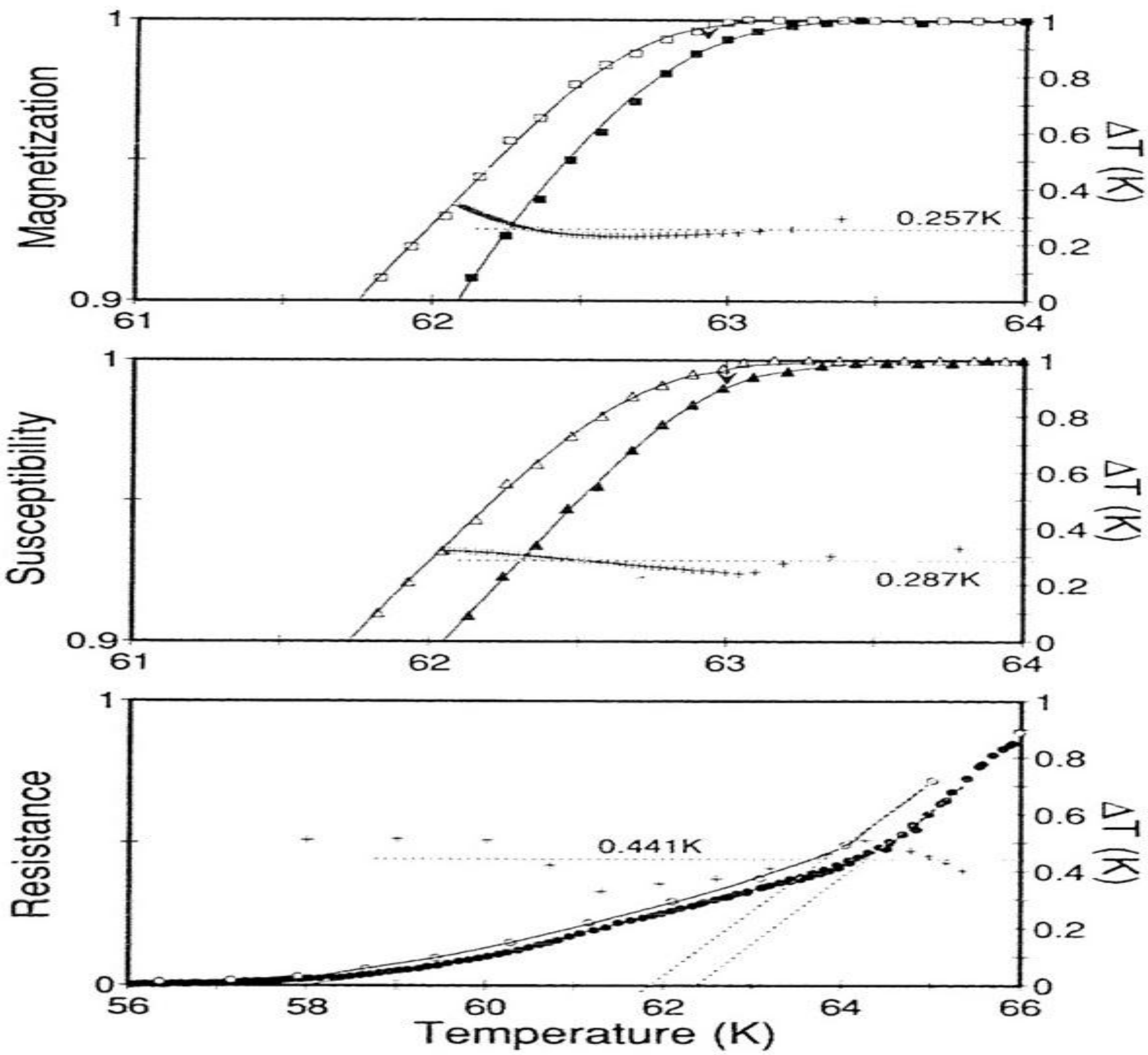

Figure 6 Oxygen isotope effect in $YBa_2(Cu_{0.975}Zn_{0.025})_3O_{7-\delta}$2.5% Zn Substitution

The empty symbols represent the ^{18}O data and the filled symbols represent the ^{16}Odata. The solid line represents the Simplex fit to the data. The "+" symbols represent the shift, ΔT_i: as a function of temperature, between the two fits to the data. The arrows on the magnetization and susceptibility graphs indicate the T_C obtained from a linear extrapolation of the bulk of the transition 54.8K for the magnetization (upper limit = 56.9K) and 55.4K (upper limit = 56.6K) for the susceptibility. No cutoff was imposed in the calculation of the mean of the isotope shift for either the magnetic or resistance measurements. The resistance measurements are normalized lo R(70K). Not all temperature scales are equivalent.

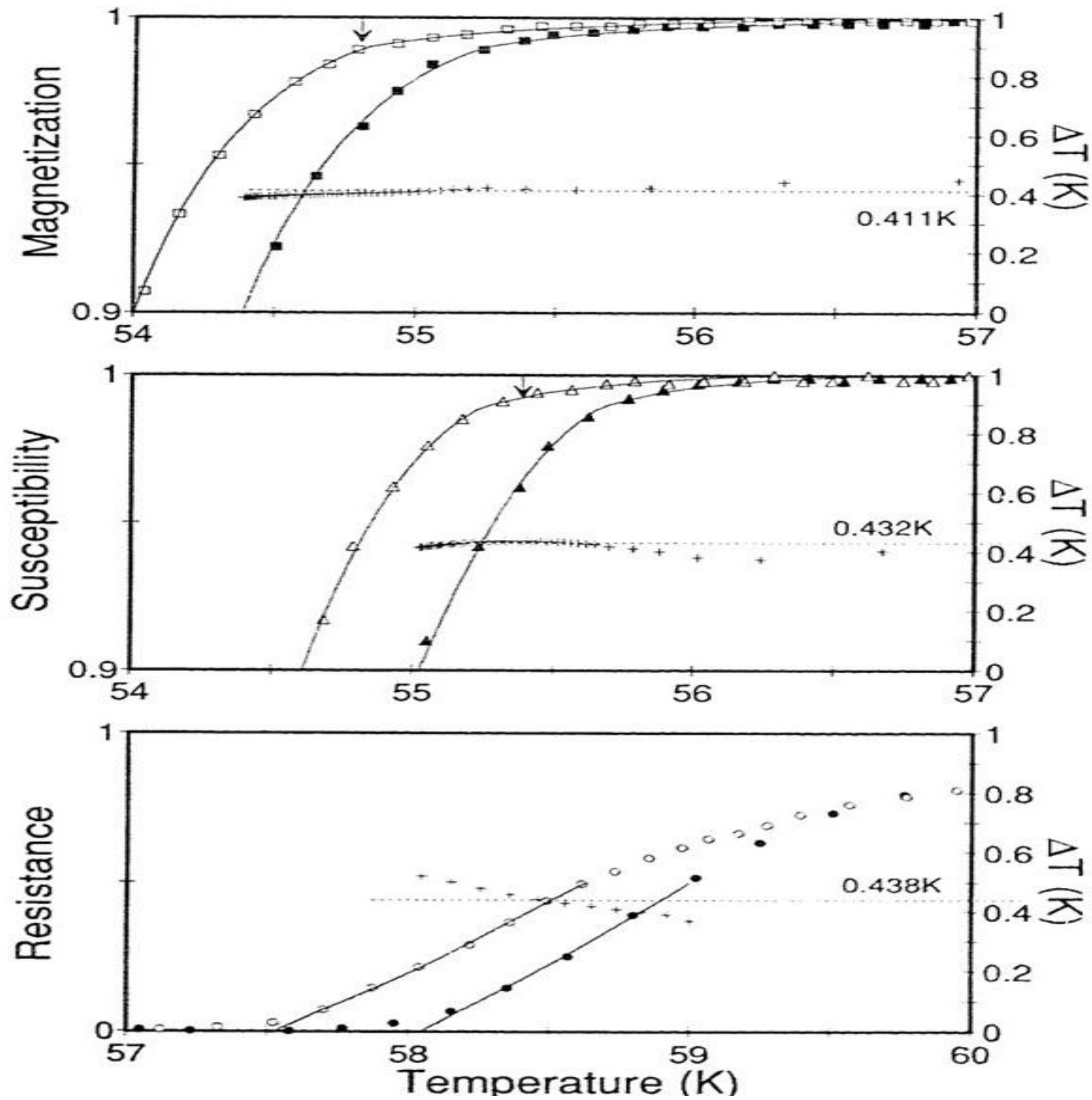

Figure 7 Oxygen isotope effect in $YBa_2(Cu_{0.96}Zn_{0.04})_3O_{7-\delta}$4% Zn Substitution

The empty symbols represent the $^{18}0$ data and the filled symbols represent the $^{16}0$ data, The solid line represents the Simplex fit to the data. The "+" symbols represent the shift, ΔTi, as a function of temperature, between the two fits to the data. The arrows on the magnetization and susceptibility graphs indicate the T_C obtained from a linear extrapolation of the bulk of the transition - 38.1K for the magnetization (upper limit = 39.6K) and 38.4K (upper limit = 39.7) for the susceptibility. No cut off was imposed in the calculation of the mean of the isotope shift for either the magnetic or resistance measurements.The resistance measurements are normalized to R(70K). Not a temperature scales are equivalent.

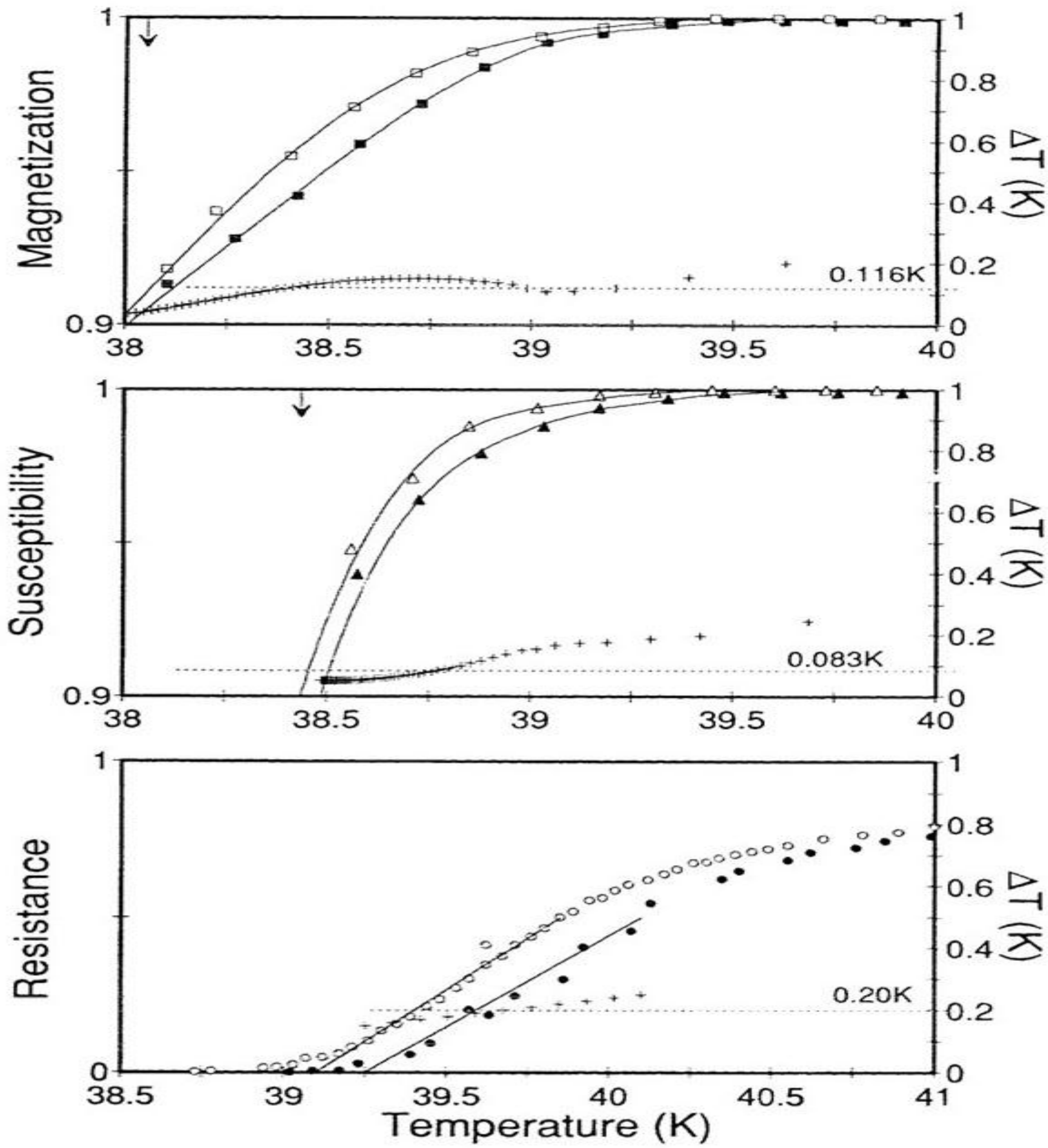

Figure .8 Oxygen isotope effect in $YBa_2(Cu_{0.95}Zn_{0.05})_3O_{7-\delta}$5% Zn Substitution

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The empty symbols represent the ^{18}O data and the filled symbols represent the $^{16}0$ data. The solid line represents the Simplex fit to the data. The "+"symbols represent the shift, ΔT_i as a function of temperature, between the two fits to the data. The arrows on the magnetization and susceptibility graphs indicate the T_C, obtained from a linear extrapolation of the bulk of the transition - 28.7K for the magnetization (upper limit = 31.4K)and 29.6K (upper limit = 31.0K) for the susceptibility. The vertical dotted line indicates the cutoff in the calculation of the mean of the isotope shift. The horizontal fine indicates this mean, and Its value is indicated above the line.

The resistance measurement are normalized to R(45K). Not all temperature scales are equivalent.

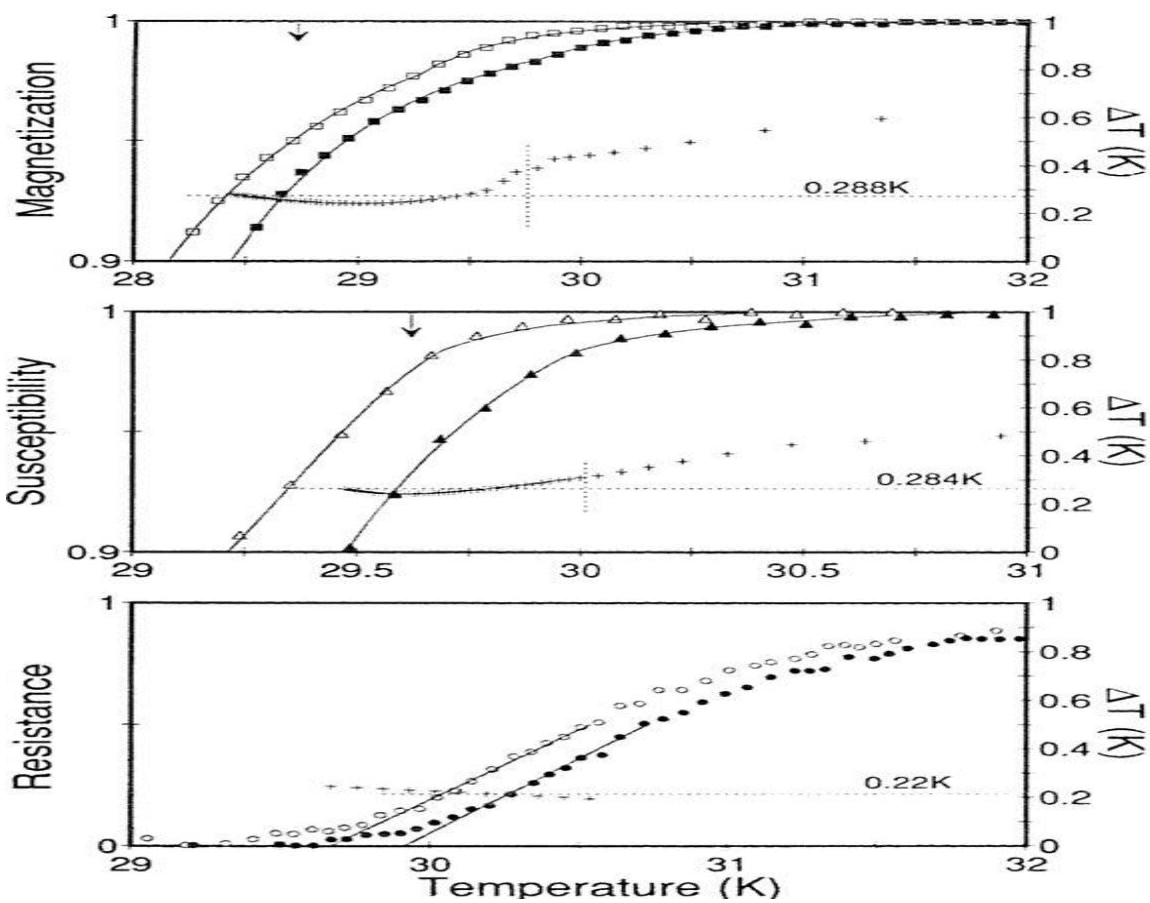

Figure 9 Oxygen isotope effect in $YBa_2(Cu_{0.94}Zn_{0.06})_3O_{7-\delta}$6% Zn Substitution

The empty symbols represent the ^{18}O data and the filled symbols represent the $^{16}0$ data. The solid line represents the Simplex fit to the data. The "+" symbols represent the shift, ΔTi; as a function of temperature, between the two fits to the data. The arrows on the magnetization and susceptibility graphs indicate the T_C obtained from a linear extrapolation of the bulk of the transition - 18.1K for the magnetization (upper limit = 21.4K) and 19.1K (upper limit = 21.8K) for the susceptibility. The vertical dotted line indicates the cutoff in the calculation of the mean of the isotope shift. The horizontal line indicates this mean, and its value is indicated above the tine. The resistance measurements are normalized to R(40K).

Not all temperature scales are equivalent.

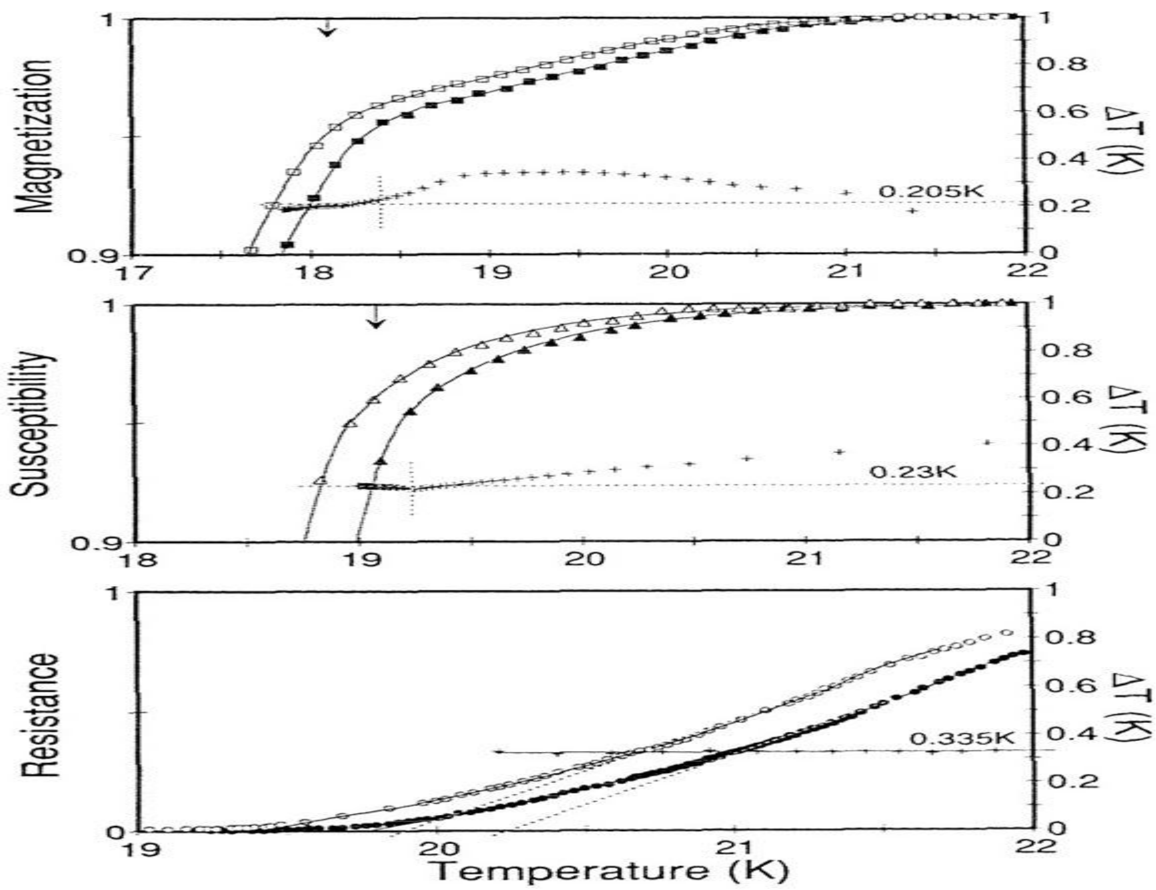

Figure 10 Oxygen isotope effect in $YBa_2(Cu_{0.93}Zn_{0.07})_3O_{7-\delta}$7% Zn Substitution 7.5% Zn Substitution

The empty symbols represent the ^{18}Odata and the filled symbols represent the ^{16}O data, The solid line represents the Simplex fit to the data. The "+" symbols represent the shift, ΔT_i as a function temperature, between the two fits to the of data. The arrows on the magnetization and susceptibility graphs indicate the T, obtained from a linear extrapolation of the bulk of the transition – 11.59Kfor the magnetization (upper limit = 14.6K) and 12.7K (upper limit = 14.8K) for the susceptibility. The vertical dotted line indicates the cutoff in the calculation of the mean of the Isotope shift. The horizontal line indicates this mean, and its value is indicated above the line. The resistance measurements are normalized R(25K). Not all temperature scales are equivalent.

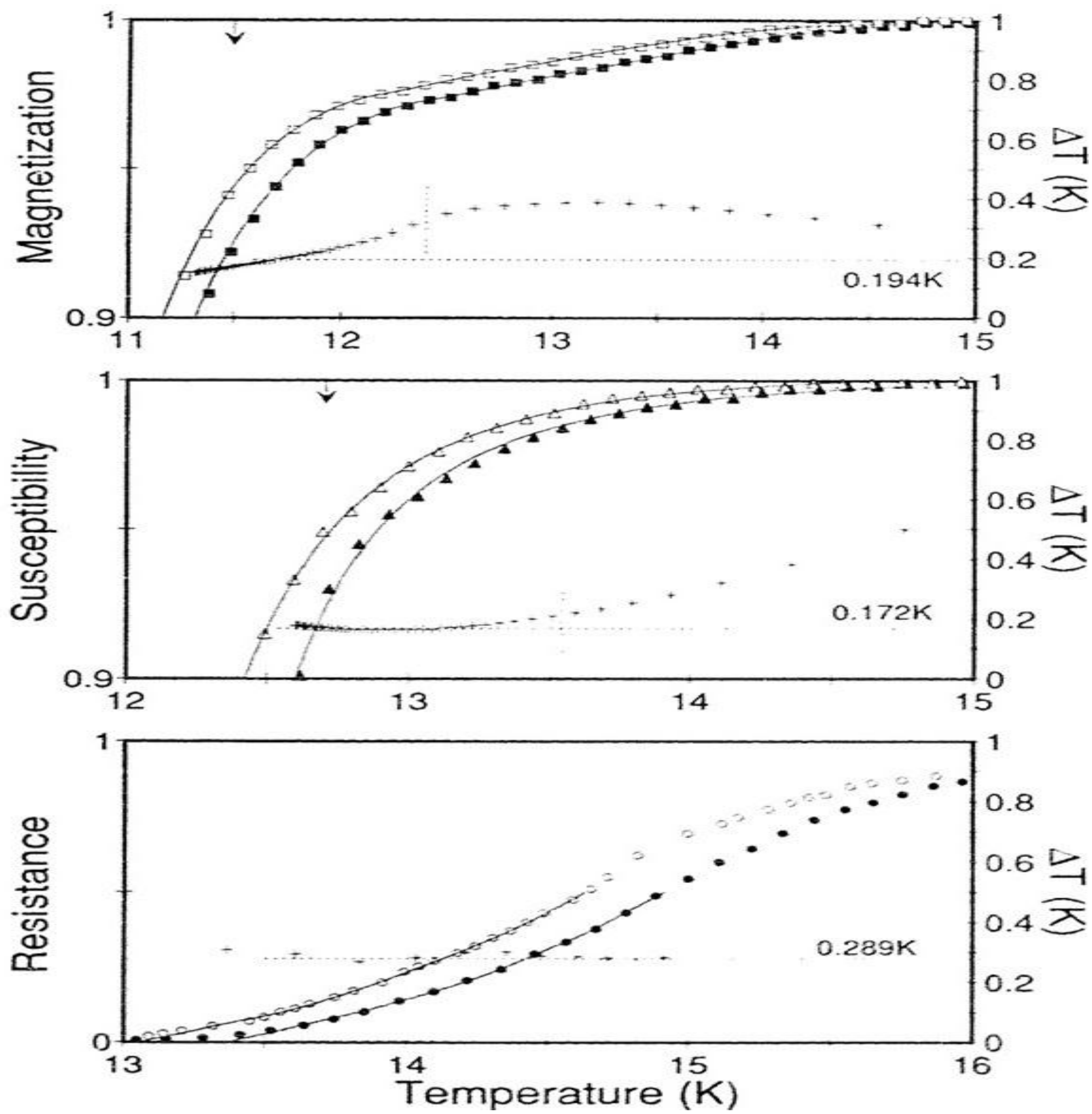

Figure 11 Oxygen isotope effect in $YBa_2(Cu_{0.925}Zn_{0.075})_3O_{7-\delta}$7.5% Zn Substitution

The empty symbols represent the ^{18}Odata and the filled symbols represent the ^{16}O data, The solid line represents the Simplex fit to the data. The "+" symbols represent the shift, ΔT_i as a function temperature, between the two fits to the of data. The arrows on the magnetization and susceptibility graphs indicate the T_C, obtained from a linear extrapolation of the bulk of the transition – 8.5Kfor the magnetization (upper limit = 11.8K) and 9.8K (upper limit = 11.3K) for the susceptibility. The vertical dotted line indicates the cutoff in the calculation of the mean of the Isotope shift. The horizontal line indicates this mean, and its value is indicated above the line.

The resistance measurements are normalized R(25K). Not all temperature scales are equivalent.

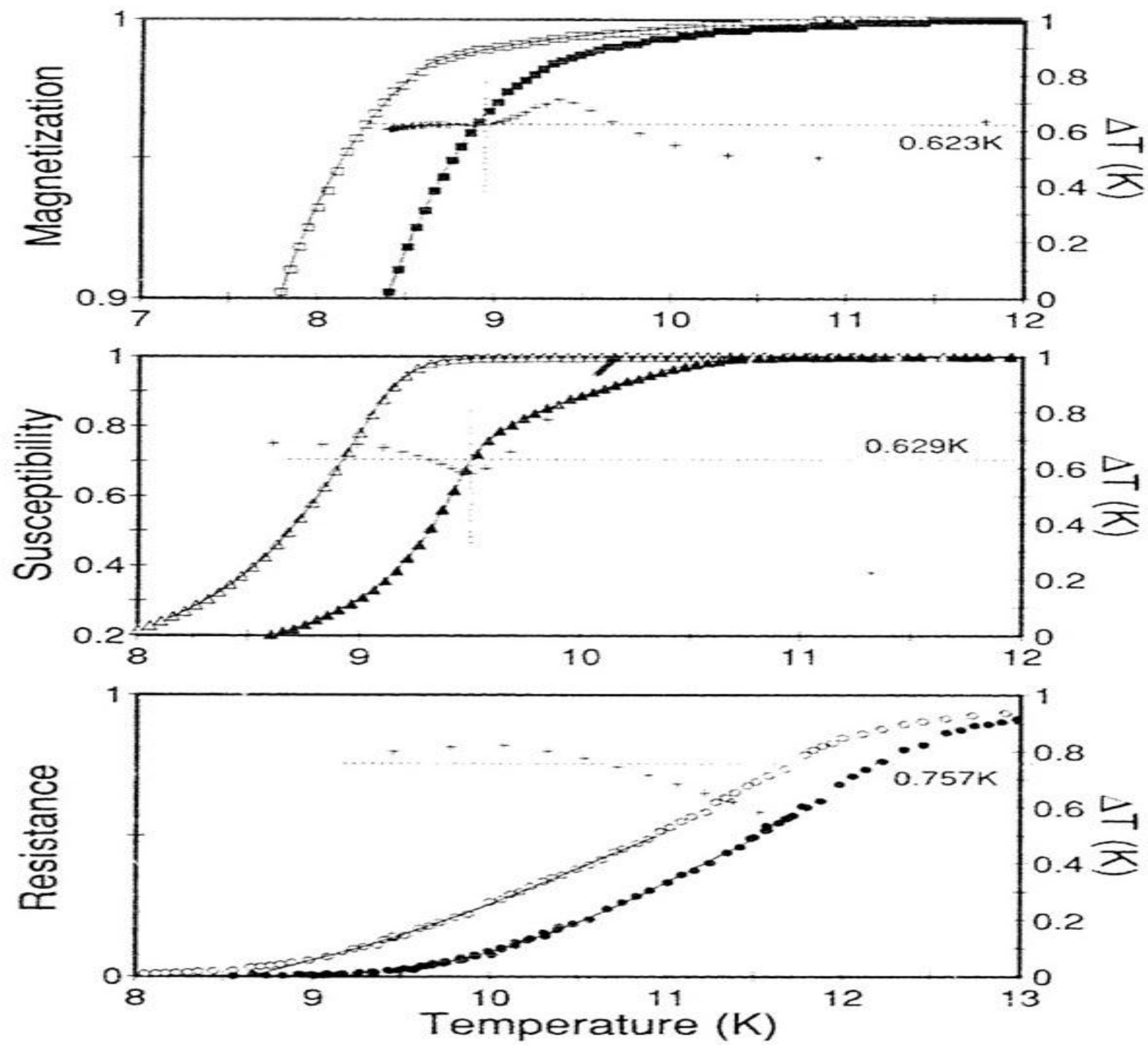

Figure 12 Oxygen isotope effect in $YBa_2(Cu_{0.92}Zn_{0.8})_3O_{7-\delta}$8% Zn Substitution

Oxygen isotope Effect in$YBa_2(Cu_{0.915}Zn_{0.085})_3O_{7-\delta}$ 8.5% Zn substitution

The empty symbols represent the ^{18}O data and the filled symbols represent the ^{16}O data. The solid line representation the Simplex fit to the data. The "+" symbols represent the shift, ΔT_i, as a function of temperature, between the two fits to the data.The arrows on the magnetization and susceptibility graphs indicate the T_C obtained from a linear extrapolation of the bulk of the transition -7.2K for the magnetization (upper limit =8.2K) and 5.6K (upper limit = 8.3K) for the susceptibility.Note the difference in the two susceptibility data. The vertical dotted line indicates the cutoff in the calculation of the mean of the isotope shift. The horizontal line indicates this mean , and its value is indicates above the lineThe resistance measurement are normalized to R(20 K).Not all temperature scales are equivalent.

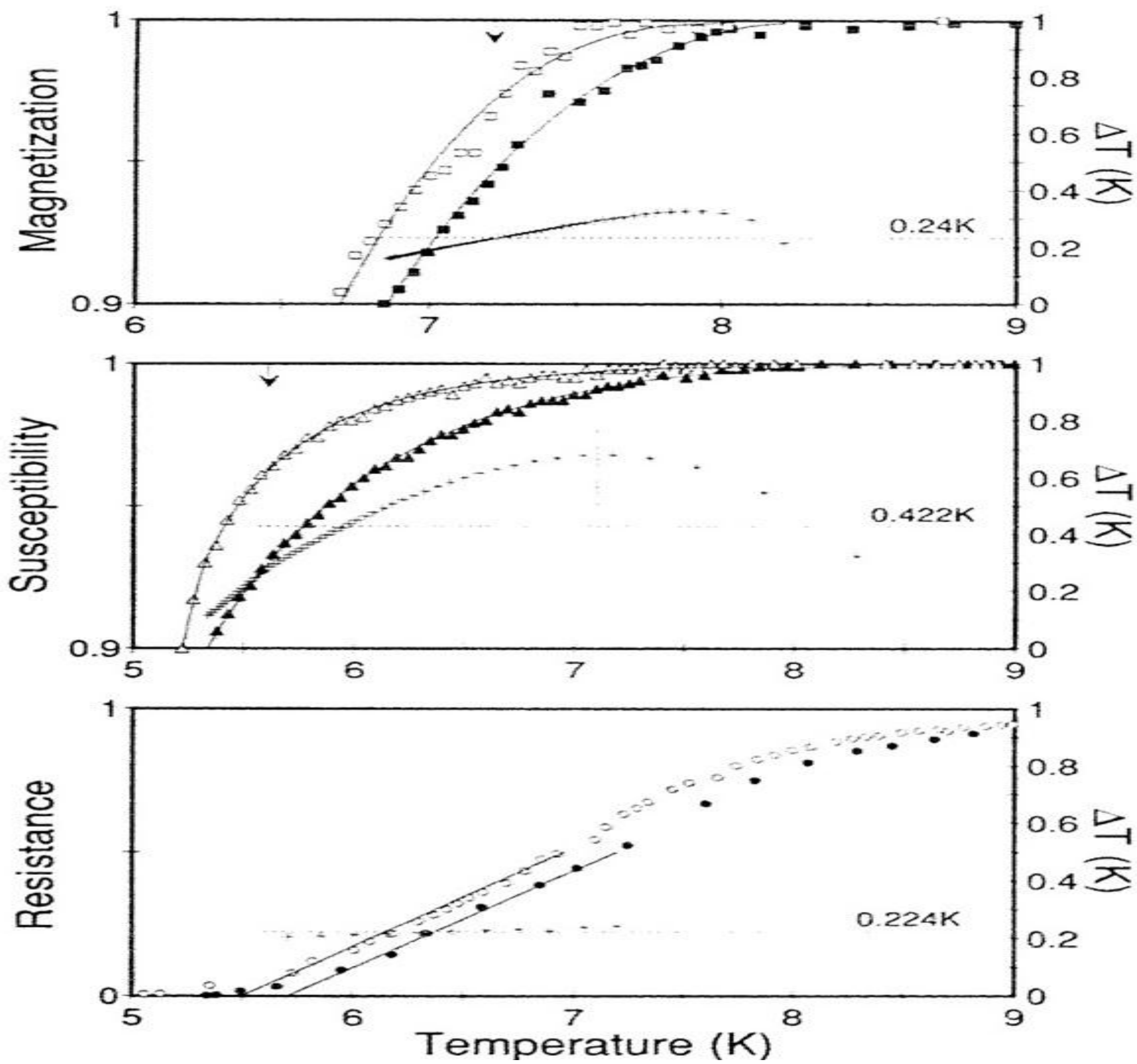

Figure 13 Oxygen isotope Effect in$YBa_2(Cu_{0.915}Zn_{0.085})_3O_{7-\delta}$8.5% Zn substitution

The empty symbols represent the ^{18}O data and the filled symbols represent the ^{16}O data. The solid line representation the Simplex fit to the data. The "+" symbols represent the shift, ΔT_i, as a function of temperature, between the two fits to the data.The arrows on the magnetization and susceptibility graphs indicate the Tc obtained from a linear extrapolation of the bulk of the transition -6.6K for the magnetization (upper limit =9.9K) and 7.7K (upper limit = 8.8K) for the susceptibility. The vertical dotted line indicates the cutoff in the calculation of the mean of the isotope shift. The horizontal line indicates this mean , and its value is indicates above the line

The resistance measurement are normalized to R(20 K).Not all temperature scales are equivalent.

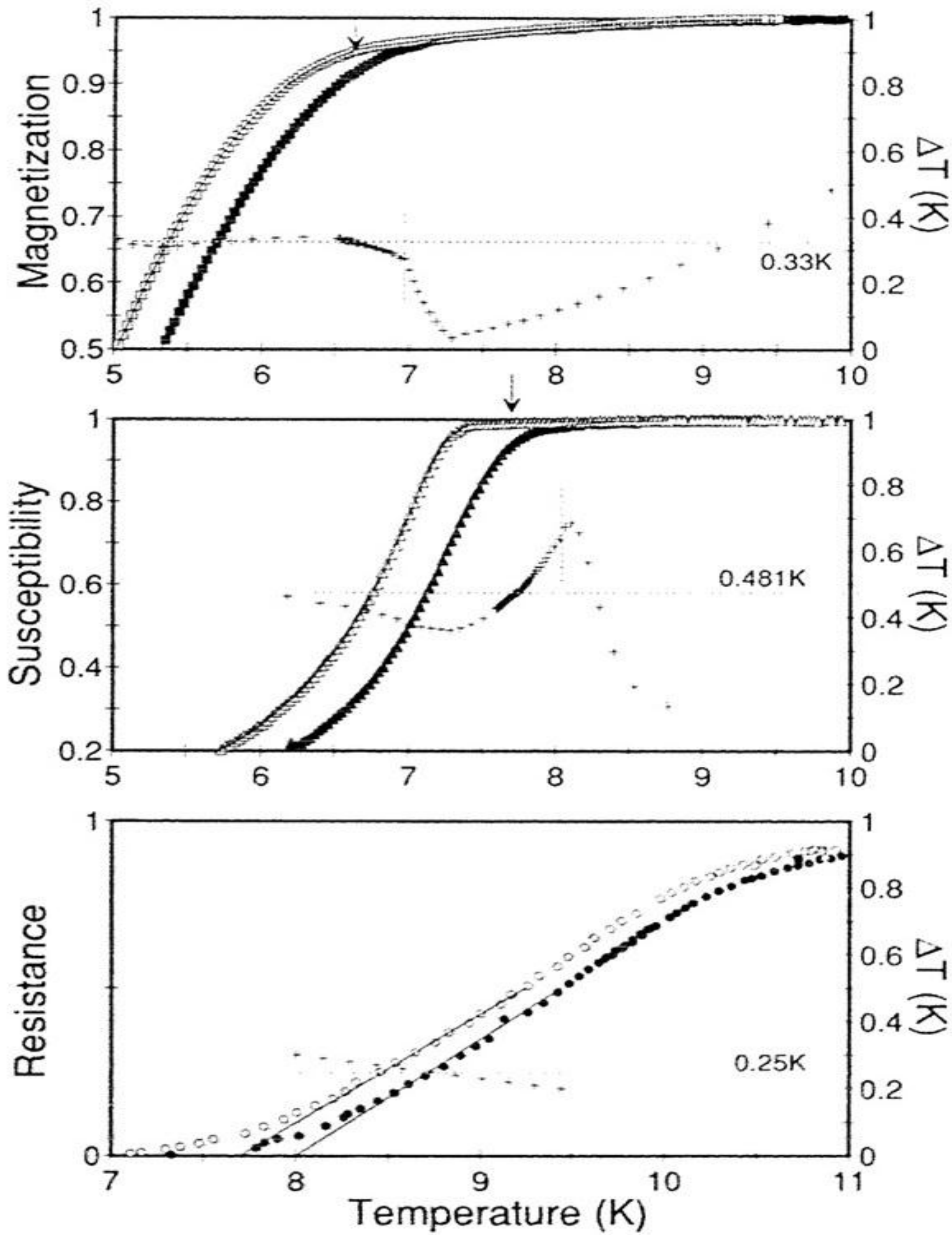

Figure 14 Oxygen isotope Effect in $YBa_2(Cu_{0.9125}Zn_{0.0875})_3O_{7-\delta}$ 8.75% Zn substitution

Measurement	Sample	T_C(K)	T_C(K)	A
dc resistance	2%	$68.1\ ^{-0.2}_{+0.6}$	0.696±0.072	0.087±0.010
	2.5%	$62.9\ ^{-0.2}_{+0.5}$	0.257±0.031	0.025±0.004
	4%	$54.8\ ^{-0.2}_{+2.1}$	0.411±0.065	0.064±0.011
	5%	$38.1\ ^{-0.2}_{+1.5}$	0.116±0.045	0.026±0.010
	6%	$28.7\ ^{-0.2}_{+1.1}$	0.288±0.032	$0.086\ ^{+0.010}_{-0.016}$
	7%	$18.1\ ^{-0.2}_{+1.0}$	0.205±0.049	$0.097\ ^{+0.025}_{-0.035}$
	7.5%	$11.5\ ^{-2.0}_{+5.0}$	0.194±0.043	$0.144\ ^{+0.035}_{-0.055}$
	8%	$8.5\ ^{-2.0}_{+5.0}$	0.623±0.033	$0.646\ ^{+0.053}_{-0.211}$
	8.5%	$7.2\ ^{-0.2}_{+2.0}$	0.240±0.052	$0.288\ ^{+0.074}_{-0.98}$
	8.75%	$6.6\ ^{-0.2}_{+1.3}$	0.330±0.040	$0.435\ ^{+0.070}_{-0.183}$
ac susceptibility	2%	$67.9\ ^{-0.2}_{+0.6}$	0.714±0.078	0.090±0.011
	2.5%	$63.6\ ^{-0.2}_{+1.0}$	0.287±0.025	0.039±0.004
	4%	$55.4\ ^{-0.2}_{+1.1}$	0.432±0.092	0.066±0.015
	5%	$38.4\ ^{-0.2}_{+0.3}$	0.083±0.044	0.18±0.010
	6%	$29.6\ ^{-0.2}_{+0.1}$	0.284±0.036	0.082±0.012
	7%	$19.1^{-0.2}_{+0.1}$	0.230±0.023	$0.103\ ^{+0.012}_{-0.016}$
	7.5%	$12.7^{-0.2}_{+0.1}$	0.172±0.020	$0.116\ ^{+0.016}_{-0.022}$
	8%	$9.8\ ^{-0.2}_{+0.1}$	0.629±0.038	$0.563\ ^{+0.048}_{-0.028}$
	8.5%	$5.6\ ^{-0.2}_{+0.1}$	0.422±0.188	$0.665\ ^{+0.325}_{-0.107}$
	8.75%	$7.7\ ^{-0.2}_{+0.1}$	0.481±0.100	$0.548\ ^{+0.137}_{-0.172}$
dc resistance	2%	$67.7\ ^{-0.2}_{+0.6}$	0.711±0.060	0.090±0.010
	2.5%	$60.2\ ^{-0.2}_{+1.0}$	0.441±0.087	0.062±0.015
	4%	$58.0\ ^{-0.2}_{+1.1}$	0.438±0.043	0.064±0.006

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	5%	$39.3\ ^{-0.3}_{+0.3}$	0.200±0.050	0.043±0.008
	6%	$29.9\ ^{-0.1}_{+0.1}$	0.220±0.082	0.062±0.012
	7%	$20.2\ ^{-0.3}_{+0.1}$	0.335±0.025	0.142±0.011
	7.5%	13.4±0.3	0.289±0.020	0.185±0.012
	8%	9.6±0.3	0.757±0.061	0.697±0.082
	8.5%	5.7±0.2	0.224±0.031	0.340±0.060
	8.75%	8.0±0.4	0.250±0.050	0.270±0.068

Table 2. T_{C}, ΔT_C and α for Zn substitued YBCO.

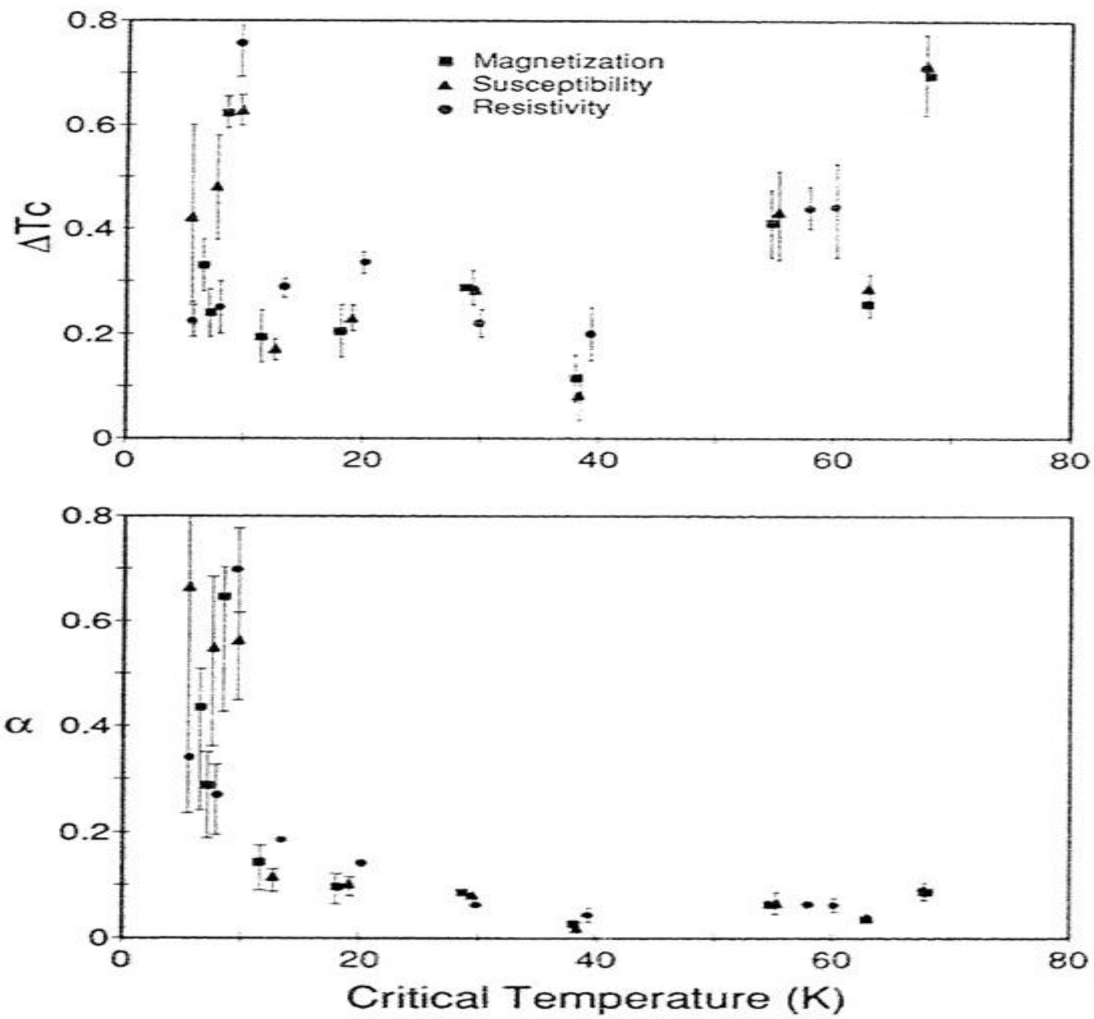

Figure15 ΔT_C and α vs. T_C for Zn substituted YBCO.

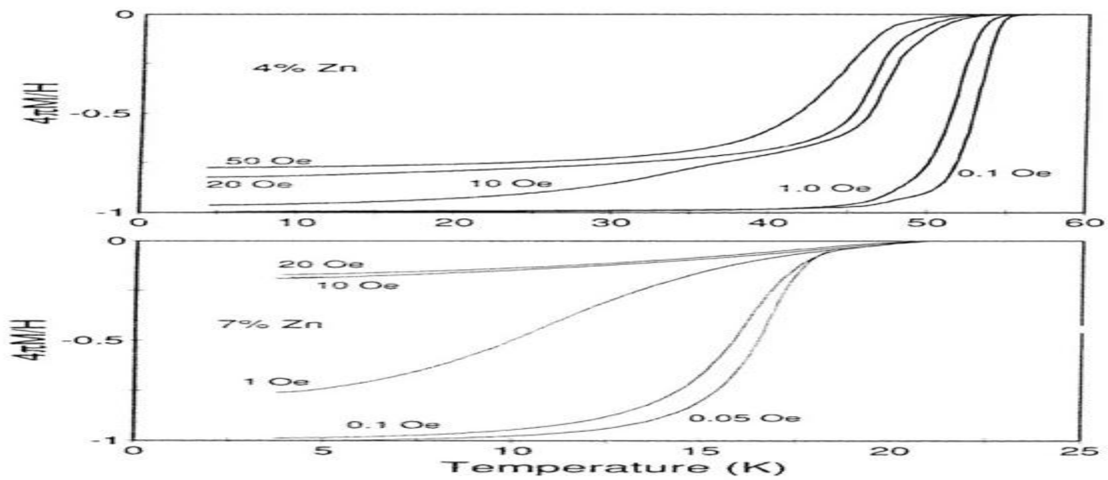

Figure 16 Field dependence of the 4% & 7% Zn substituted YBCO sample.transition characteristics.

Below this field, the penetration effects are small and above this flied the penetration effects saturate. For the 4% Zn sample, this field is Rear H = 10Oe and for the 7% Zn it occurs near H = 1Oe. A logarithmic plot of -4πM/H vs. temperature (Figure 17) for the different measuring flied strengths shows that the strong field dependence still remains in the top 10% of the transition. There does, however, appear to be some convergence to a common Tc, Near the onset of superconductivity the level of noise begins to overwhelm the change in signal and it becomes difficult to determine if all fields converge to t h e same point. The noise is proportionally less for the higher fields and if we take T_C, as the point at which the signal emerges from tire noise, there is good agreement between the T_C's for t h e different fields. The isotope shift has been calculation for fields of H =0.05, 1, 10, 20 and 50Oe for the 4% Zn and 7% 2% data (Figure 8.18). Front this data we can see no clear dependence in the shift.

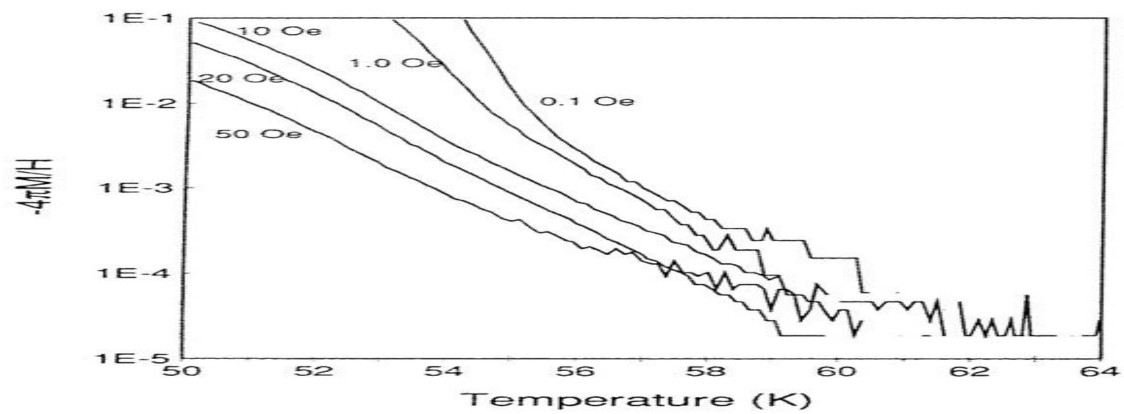

Figure 17 Log (-4πM/H) vs. T showing convergence near T_C as a function of applied field .All curves are ZFC magnetization measurements performed on the ^{16}O samples.

The isotope shift in the 4% and 7% Zn substituted sample at different applied measuring fields. The filled symbols represent the ^{16}O isotope data and the empty symbols represent the ^{18}O isotope data. The solid line is the Simplex fit to the dataThe filled symbols not fitted are the computed isotope shifts for the specified applied measuring fields.

All data are ZFC magnetization measurements.

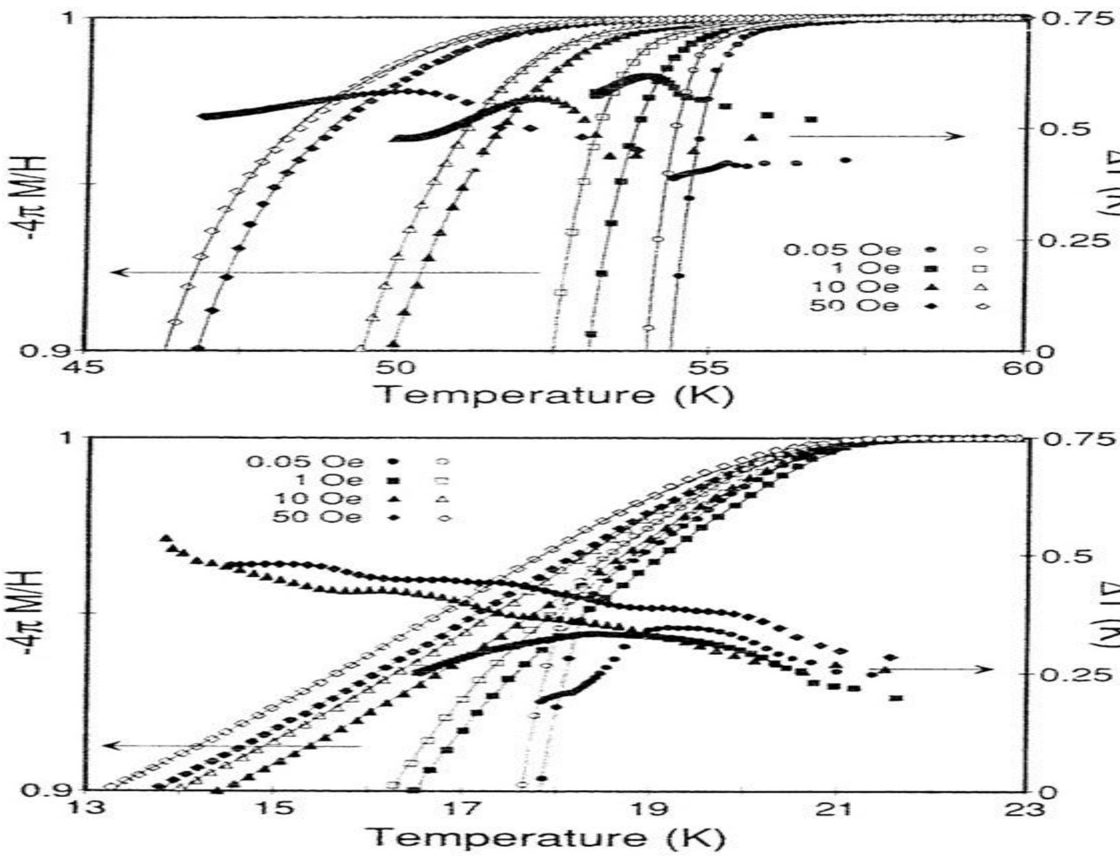

Figure 18

DISCUSSION

The magnetization data was corrected for effect of fields penetration at low temperature by taking into account the cross sectional area (moloar volume) of the sample and the magnitude of the ac susceptibility and comparing them with the 2% Zn Sample. The corrected magnetization (Figure 8.19) is unaffected to with a few percent on all but the lowest T_C samples at Zn concentration of 8%.8.5% and 8.75%.The pentration of the measuring fields into the sampe with a low T_C means that the comlete explusion of the magnetic flux from the samples, at the lowest tempertature obtainable in the magnetometer(4K),is not possible. Thus even in a field as low as 0.05Oe a tempertaure sweep from 4K to above Tc does not represent a full scale transitions .It is clear that lower the critical tempertaure, the greater this effect becomes. This will then affect any calculation of the meissner effect on the sample with a low Tc, which accounts for the lage diffrence (between $^{18}O/^{16}O$ pairs) in the Messiner fraction for the 8%,8.5%and 8.75 Zn concentration reported in Table 8.1. the lack of correlation between the Messiner fraction for the different isotope (8%,8.5%and8.75%) indicate that the effect measuring field has on each isotpe is also different. As the shape of the 8%, 8.5% and 8.75% tranistions are already affected by the penetrations of the measuring fields , normalizing the tranisitions in order to compute the isotope shift will likely create an even larger error in obtaining a value of ΔT_C and hence α for these samples. It would be wrongs to surmise that the actual shift shoukd be larger than measured as was done for the 50% Pr samples. In those sample, the effect of a premature field penetration were

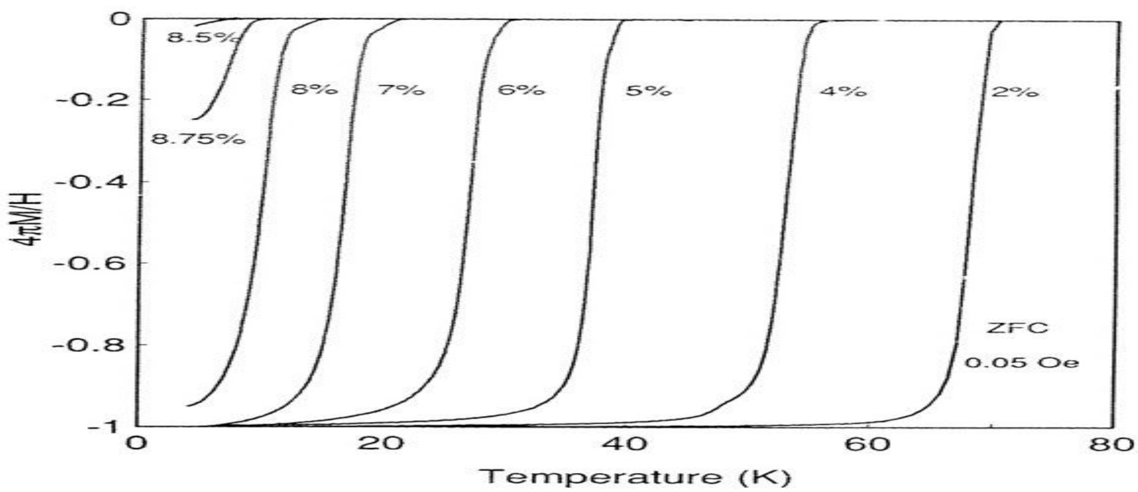

Figure 19 DC magnetizations vs. temperature for Zn substituted YBCO.

The magnetization has been corrected for moral volume and field strength. Note that the low Tc material do not give full transitions. small and the shape of the transition was preserved. In the 8% Zn sample however, there is not even a hint of the characteristic low temperature tail in the ^{16}O sample transition (Figure 8.4). It is clear that at 4.2K, the transition has already begun. The field measurements on the 7% and 4% samples indicate that a measuring field of 10Oe and 1Oe respectively has a distorting effect on the shape and size of the transition. Clearly, a measuring field of 0.050e with be sufficient to have a large distortion effect on the even lower T_C, samples of 8%, 8.5% and 8.75% Zn. For these samples, the shift obtained from the resistive measurements will be more accurate. In two of these samples, 8.5% and 8.75% Zn, the resistance measurement does not give the large shift obtained from the magnetic measurements but instead gives the same constant shift noted for the other samples. The large isotope shift in the 8% Zn samples cannot be explained. Both the magnetic and the resistive measurements are in agreement. It seems unreasonable for this concentration to present such a large shift in view of the results of the other concentrations. To alleviate the problems of field penetration, many groups measure the isotope shift on the FC data as opposed to the ZFC data as we do. In most of the cases, we do not believe this is a problem because the isotopic shift is the same (Figure 8.20) for the reversible/irreversible regime of the data. However, our experimental setup does not have the temperature accuracy for measurements decreasing in temperature (FC) as it does for those increasing in temperature (ZFC).

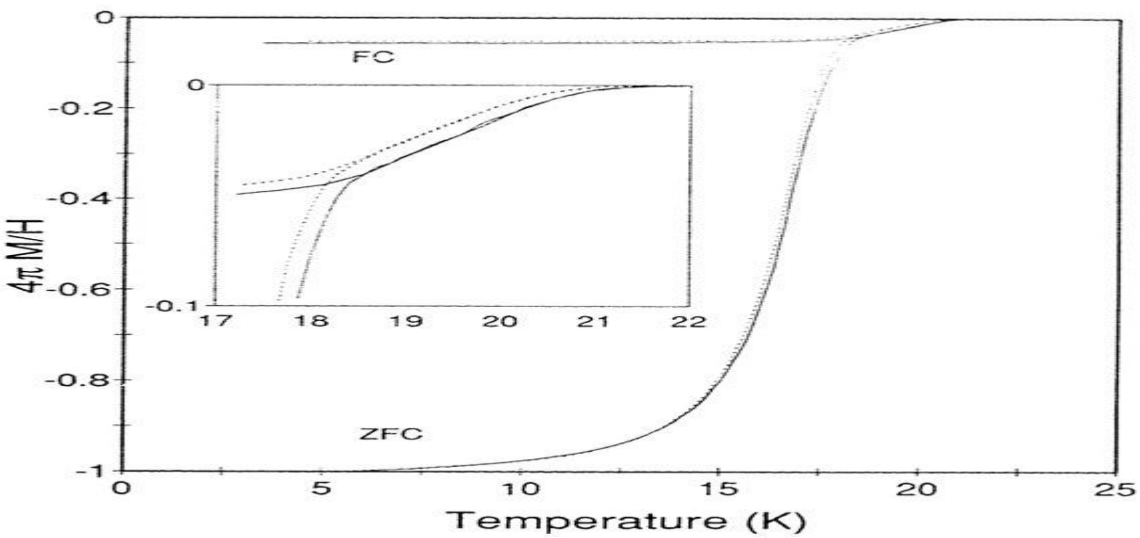

Figure .20

Relationship between the isotope effect and the reversible- irresolvable point of the magnetic transitions. Inset is an enlargement of the point of separations of the ZFC data from the FC data. Solid lines are ^{16}O isotope and dashed are the ^{18}O isotope .Measurements were made on the 7% Zn substituted samples at a field strength of 0.05Oe.

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