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The Possible Occurrence of Multi-Phase Behavior in the  
High  $T_c$  Superconductor  $YBa_2Cu_3O_x$ .

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Following the discovery of superconductivity with  $T_c > 90$  K in the Y-Ba-Cu-oxide system<sup>1,2</sup> and the subsequent identification of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  as the superconducting component<sup>3-7</sup> a number of neutron powder diffraction investigations<sup>8-13</sup> reported the structure of this phase and details of the oxygen atom ordering as shown in Fig. 1. The final refinements in all these powder neutron diffraction investigations consistently show considerable residual scattering at the same diffraction peaks. In some cases shoulders are observed on some diffraction peaks ( in particular the 004 reflection<sup>8</sup>, see Fig. 2 ) which cannot be accounted for by effects such as line broadening or reduction in unit cell symmetry. Furthermore, all data refinements result in a model with an unusually large temperature factor for the oxygen atom O1, which is not seen to scale with temperature<sup>9,10</sup>. This apparent anomalous behavior may have a physical origin in the vibrational amplitude of O1, or may be due to structural features not correctly accounted for by the structural model. Thus, while the structural model previously presented<sup>8-13</sup> provides a satisfactory fit for the diffraction data we have continued to search for alternate structure models which better represent the experimental data.

The oxygen atom stoichiometries as derived from the different diffraction experiments vary from  $\text{YBa}_2\text{Cu}_3\text{O}_7$ <sup>10,13</sup> to  $\text{YBa}_2\text{Cu}_3\text{O}_{6.6}$ <sup>12</sup>. Determinations of the oxygen content of superconducting samples by hydrogen reduction<sup>9,12</sup> and by chemical analysis<sup>14-16</sup> give comparable results. Despite the wide range of oxygen contents reported in these samples a  $T_c > 90$  K was consistently reported. Accurate studies of the

variations in  $T_c$  with oxygen content<sup>16-19</sup> have shown that  $T_c \approx 90$  K for oxygen contents ranging from  $x = 7.0$  to  $\approx 6.7$  and rapidly decreasing to  $T_c \approx 55$  K for  $x \approx 6.7$  to  $6.5-6.4$  with lower oxygen contents giving non-superconducting samples. One possible explanation for the occurrence of this step like behavior of the  $T_c$  with decreasing oxygen contents is the occurrence of discrete multiple phases of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  possessing different oxygen contents and different superconducting transition temperatures. Such predictions have come from theoretical studies<sup>20</sup> and thermodynamic considerations<sup>21</sup>. We report here the results obtained for powder diffraction studies on four  $\text{YBa}_2\text{Cu}_3\text{O}_x$  samples in which a model with two orthorhombic phases was used to obtain an improved agreement. The implications of this structural model on the systematic variation of  $T_c$  with oxygen content will be discussed.

Samples of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  were synthesized by three different methods: samples 1 and 2 were prepared by mixing, grinding and sintering  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  as previously reported<sup>4</sup>, sample 3 was prepared by decomposition of nitrate salts<sup>22</sup>, and sample 4 was synthesized by the decomposition of a carbonate co-precipitate<sup>23</sup>. Neutron powder diffraction data were collected using the special-environment powder diffractometer at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory and refined using the Rietveld structure refinement technique<sup>24</sup>.

Models used in the structure refinement include: doubling of the a and b axes to give  $2a \ b \ c$  and  $a \ 2b \ c$  supercells ( ie. oxygen vacancy ordering ); a mixture of one orthorhombic,  $Pmmm$ , phase with a cubic perovskite cell ( presumably resulting from incomplete ordering of  $\text{Y}^{3+}$

and  $Ba^{2+}$  cations); orthorhombic  $YBa_2Cu_3O_x$  and tetragonal,  $P4/mmm$ ,  $YBa_2Cu_3O_x$  ( with  $x < 6.5^{22}$  possibly due to an incomplete tetragonal-orthorhombic phase transition on cooling from high temperature); and two nearly identical orthorhombic phases of  $YBa_2Cu_3O_x$  where individual scale factors, unit cell constants, peak shapes, atom positions and oxygen vacancies were allowed to vary individually for each phase. The supercell models which allow more variable parameters produced agreement factors nearly identical to those resulting from a one-phase model. Of the models which include mixed phases only the model with two orthorhombic phases produced substantially better agreement factors as given in Table I. With the large number of observations used in these studies the improvements in the R-factors are statistically significant at the 99.9+% level<sup>25</sup>. Parameters derived from the study are presented in Table II. The final observed and calculated neutron powder diffraction profile for two orthorhombic,  $Pmmm$ , phases of  $YBa_2Cu_3O_x$  and a small fraction of  $CuO$  present in all samples given in Fig. 2 shows that the residuals in the fit are significantly decreased by the use of this model. This is the only model used which correctly reproduces the shoulder on the 004 peak (see insert on Fig. 2). Furthermore, the O1 temperature factor, while still remaining large now scales with temperature. As is shown in Figure 3, the value of  $B_{iso}$  for O1 at 10 K is 0.60 as compared to 1.3-1.4  $\text{\AA}^2$  at 298 K. Most significantly, the oxygen stoichiometries determined by the neutron refinement consistently show that the samples are mixtures of one phase with composition  $YBa_2Cu_3O_7$  and a second phase ( or phases ) with composition  $YBa_2Cu_3O_x$ ,  $x < 7.0$ . Peak widths of these two phases as indicated by the sigma-1 values in Table

It are consistent with sharp peaks resulting from the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase and broader diffraction maxima resulting from the phase or phases with average composition  $\text{YBa}_2\text{Cu}_3\text{O}_x$ . We therefore propose that the high  $T_c$  Y-Ba-Cu-oxide superconductors are mixtures of a  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase and one or more phases with lower oxygen contents.

One possible model for the step-like variations in  $T_c$  based on the structural changes with oxygen content<sup>18</sup> postulates that the  $\text{CuO}_3$  chains serve the function of linking the  $\text{CuO}_2$  planes in the 92 K  $T_c$  material. Then as oxygen atoms are removed from the chains the inter-planer coupling decreases until the point at which the planes no longer interact through the chains. The result is a material electronically similar to  $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$  which possess a  $T_c$  of  $\approx 55$  K under applied pressure<sup>26</sup>. Thus, the initial 92 K plateau in the  $T_c$  vs oxygen content curve is postulated as resulting from the coupled behavior of the three layer system, and the 55 K step as the occurrence of superconductivity only in the planes.

The diffraction results presented here can be interpreted to provide a alternate model for the occurrence of  $T_c$  plateaus. For samples with nominal oxygen contents near 7.0 the 92 K  $T_c$  can be ascribed to the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase in a multi-phase mixture. It is suggested that as the nominal oxygen content is lowered from 7.0, that in fact there is a decrease in the amount of the  $\text{O}_7$  phase, but that it is still the presence of some of this phase which permits a 92 K  $T_c$  over an apparent stoichiometry range. At lower oxygen contents ( $x < 6.7$ ) this phase is no longer present in sufficient quantity and a 55 K  $T_c$  is observed for the remaining phase or phases. Theoretical studies have predicted a critical dependence of the band structure and resultant density of

states values on the Cu1-O4 distance<sup>27</sup> and or interplaner spacing<sup>28</sup>, which is closely related to the c-axis length. Neutron diffraction studies on quenched samples<sup>16,18</sup> have shown that the Cu1-O4 distance decreases and the c-axis length and interplanar spacing increase with decreasing oxygen content. These observations are consistent with the changes in parameter values presented in Table II for the secondary, oxygen deficient phases of  $\text{YBa}_2\text{Cu}_3\text{O}_x$ . Thus although the electronic origin of the 55 K plateau is the oxygen deficient phase (or phases), the initial 92 K plateau may result from the occurrence of mixed phase behavior in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  with 92 K superconductivity ascribed to the occurrence of a stoichiometric  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase.

We have shown evidence that the high- $T_c$  Y-Ba-Cu-oxide superconductors are mixtures of a  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase and one or more phases with lower oxygen contents. This structural model provides a possible explanation of the systematic variations in  $T_c$  with oxygen content. Further neutron and X-ray powder diffraction studies of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  materials at higher resolution are underway to confirm the existence of multi-phase behavior.

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## Figure Captions:

Fig. 1. Structure and atom numbering scheme for orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_x$ .

Fig. 2. Powder neutron diffraction data for  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , where a Rietveld profile refinement has been done assuming that the sample is a mixture of two orthorhombic phases and a small amount of  $\text{CuO}$ . The insert, upper right, is a detail of the 004 peak.

Fig. 3. Variations in the O1 temperature factor with temperature as derived from a two phase model show a decrease in the temperature factor as opposed to the results which are observed for one phase fits.

Table I. Agreement Factors for 1 and 2-Phase Fits for  $\text{YBa}_2\text{Cu}_3\text{O}_x$  Samples

	<u>Sample 1</u>		<u>Sample 3</u>	
	1 Phase	2 Phases	1 Phase	2 Phases
Structure Factor R	4.4	3.9	4.5	4.0
Weighted Profile R	5.9	4.8	5.6	5.1
Expected R	3.5	3.5	1.9	1.9
Refined Parameters	34	48	39	48
Degrees of Freedom	3665	3651	3660	3651
Rw(1 phase)/ Rw(2 phases)	1.23		1.10	
Ratio Limit for 99.5 % Probability	1.007		1.007	

Table II. Fractional atomic coordinates, thermal parameters, and peak shape parameters for YBa<sub>2</sub>Cu<sub>3</sub>O<sub>x</sub>, space group Pmmm.

Phase 1 YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub>

	Sample 1	Sample 2	Sample 3	Sample 4
Unit Cell Parameters (Å)				
a	3.8214(1)	3.8205(1)	3.8227(2)	3.8240(1)
b	3.8878(1)	3.8880(1)	3.8882(1)	3.8900(1)
c	11.6822(3)	11.6825(4)	11.6788(4)	11.6782(4)
V <sub>c</sub> Å <sup>3</sup>	173.561(4)	173.532(5)	173.585(6)	173.717(4)

Fractional Atomic Coordinates\*

Ba ( z )	0.1838(4)	0.1833(5)	0.1823(5)	0.1830(4)
Cu2 ( z )	0.3546(2)	0.3532(3)	0.3522(4)	0.3548(2)
O2 ( z )	0.3776(3)	0.3785(4)	0.3782(4)	0.3779(3)
O3 ( z )	0.3772(3)	0.3756(4)	0.3746(5)	0.3763(3)
O4 ( z )	0.1589(4)	0.1587(5)	0.1584(5)	0.1590(4)

Thermal Parameters ( B<sub>iso</sub> Å<sup>2</sup> )\*\*

Y	0.40(3)	0.37(3)	0.49(3)	0.39(3)
Ba	0.52(4)	0.50(3)	0.56(3)	0.57(3)
Cu1	0.49(3)	0.52(3)	0.77(4)	0.57(3)
Cu2	0.26(2)	0.19(2)	0.27(2)	0.27(3)
O1	1.44	1.29	1.41	1.36
O2	0.45(3)	0.50(3)	0.50(3)	0.47(3)
O3	0.36(4)	0.31(4)	0.38(4)	0.35(3)
O4	0.72(4)	0.70(5)	0.90(6)	0.77(4)

Peak Shape Parameters\*\*\*

Σ <sub>1</sub>	61(2)	35(2)	53(3)	53(2)
Σ <sub>2</sub>	2.7(5)	1.6(4)	4.0(6)	3.8(5)

<u>Phase 2</u>	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.69</sub>	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.82</sub>	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.42</sub>	YBa <sub>2</sub> Cu <sub>3</sub> O <sub>6.66</sub>
	Sample 1	Sample 2	Sample 3	Sample 4
Vol.(Phase2)/Vol.(Phase1)	0.20	0.40	0.70	0.24
Unit Cell Parameters (Å)				
a	3.8396(5)	3.8298(5)	3.8310(4)	3.8377(4)
b	3.8785(4)	3.8844(3)	3.8835(3)	3.8809(3)
c	11.6677(12)	11.6747(9)	11.6768(9)	11.6709(10)
V <sub>c</sub> Å <sup>3</sup>	173.76(2)	173.68(2)	173.72(2)	173.82(2)
Fractional Atomic Coordinates*				
Ba (z)	0.1852(17)	0.1865(11)	0.1896(9)	0.1872(12)
Cu2 (z)	0.3618(11)	0.3627(8)	0.3656(8)	0.3605(8)
O2 (z)	0.3745(15)	0.3746(10)	0.3732(8)	0.3747(11)
O3 (z)	0.3907(14)	0.3886(10)	0.3899(10)	0.3883(10)
O4 (z)	0.1574(16)	0.1598(12)	0.1601(10)	0.1578(13)
Occupation Factors****				
O1	0.58(9)	0.82(4)	0.61(5)	0.68(4)
O4	2	2	1.81(2)	1.92(5)
O5	0.11(5)	0.00(4)	0.00(2)	0.06(3)
Peak Shape Parameters***				
Σ <sub>1</sub>	197(15)	87(6)	92(5)	127(8)
Σ <sub>2</sub>	5(3)	0.7(2.2)	-23(4)	4(3)
Σ <sub>3</sub>	-176(26)	-48(13)	158(27)	-75(20)

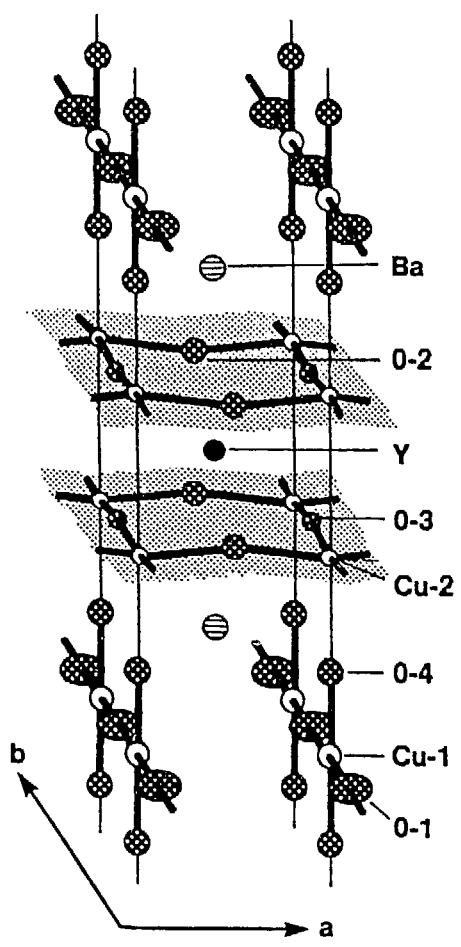
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Atom positions are: Y (.5 .5 .5), Ba (.5 .5 z), Cu1 (0 0 0), Cu2 (0 0 z), O1 (0 .5 0), O2 (.5 0 z), O3 (0 .5 z), O4 (0 0 z) and O5 (.5 0 0).

\*\* Anisotropic temperature factors were used for atom O1. Temperature factors for phase 2 are constrained to be equal to those of phase1 with the temperature factor for O5 equal to that for O1.

\*\*\* Σ<sub>3</sub> (anisotropic strain broadening term ) included for Phase 2 only.

\*\*\*\* All positions in Phase 1 were fully occupied and the population of O5 refined to zero. Occupations within 1 esd of full occupation were set to their nominal values.



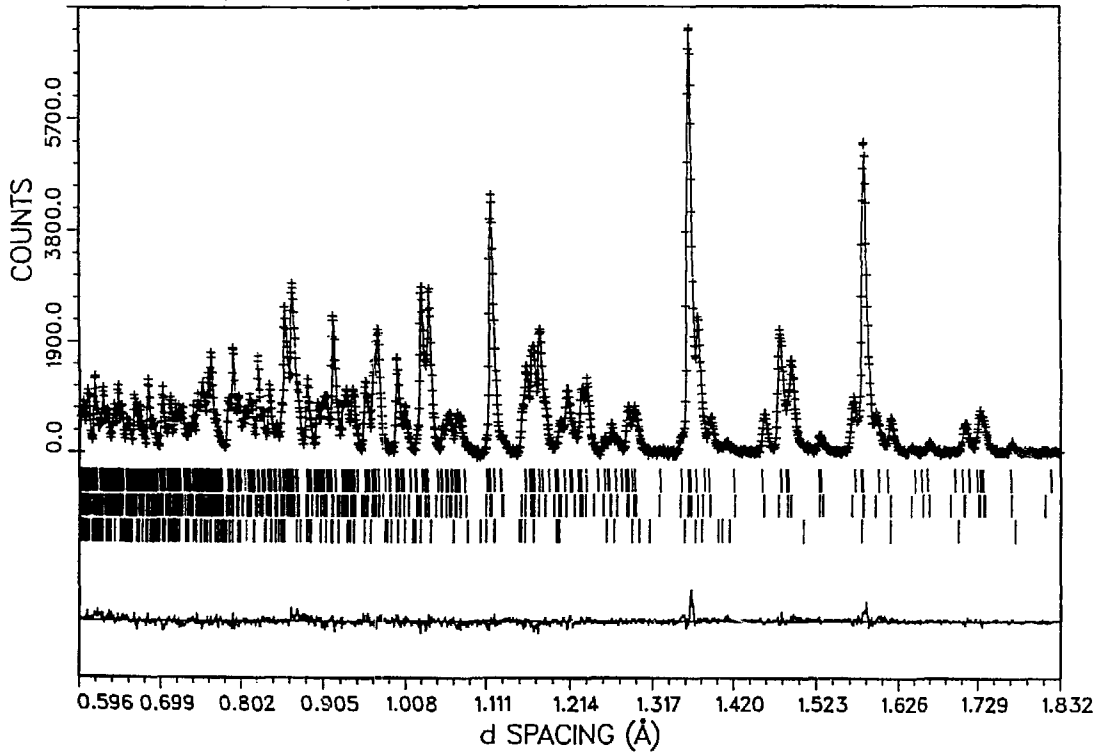
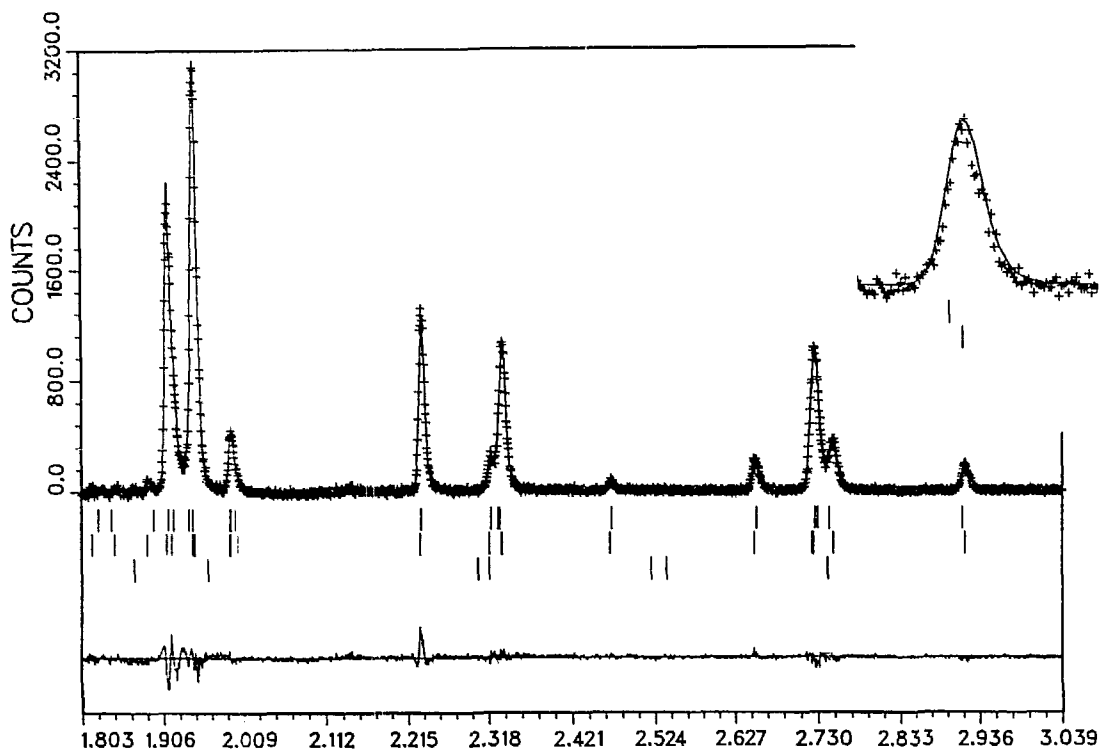




Figure 3. Variation in the O1 Temperature Factor with Temperature.

