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THERMODYNAMIC BEHAVIOR OF HIGH-T_c OXIDE SYSTEMS VIA EMF AND RELATED MEASUREMENTS*

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ABSTRACT

EMF measurements of oxygen fugacities as a function of stoichiometry have been made in the $YBa_2Cu_3O_x$, $NdBa_2Cu_3O_x$, and $Nd_{1.81}Ce_{0.19}CuO_x$ superconducting systems in the temperature range 400-750°C by means of an oxygen titration technique with an yttria-stabilized zirconia electrolyte. The object of our current measurements is to investigate the effect of ionic size of Y, Gd and Nd on the thermodynamic behavior and structural transitions in the $LnBa_2Cu_3O_x$ system. The shape of the 400°C isotherm for $NdBa_2Cu_3O_x$ suggests the presence of a miscibility gap at lower temperatures, at values of x that are higher than those in the $YBa_2Cu_3O_x$ system. The locations of the miscibility gaps are consistent with the effects of ionic radii on the composition dependence of T_c for these systems. Our results explain the two plateaus in measured values of T_c as a function of composition for the $YBa_2Cu_3O_x$ system and appear to be consistent with the less pronounced T_c plateaus found for the $NdBa_2Cu_3O_x$ system at higher stoichiometry values. For a given oxygen stoichiometry, partial pressures of oxygen above $NdBa_2Cu_3O_x$ are higher than for the $YBa_2Cu_3O_x$ system in accord with calculated partial molar thermodynamic quantities. The results of limited measurements on the n-type (electron -doped) superconducting $Nd_{1.81}Ce_{0.19}CuO_x$ system will be presented.

A thermodynamic assessment and intercomparison of our oxygen partial pressure measurements with the results of other measurements will be presented.

INTRODUCTION

The importance of oxygen stoichiometry on the superconducting behavior of oxide systems containing copper has been emphasized in numerous studies, particularly on the promising $YBa_2Cu_3O_x$ system. Based on neutron diffraction studies on $YBa_2Cu_3O_x$, it has been established that two structures exist: an orthorhombic structure and a tetragonal structure.[1] The orthorhombic structure has been identified as being responsible for the high T_c behavior; the tetragonal structure is not superconducting. Briefly, the two structures differ in the distribution of oxygen, atoms, and vacancies over the lattice sites of the basal plane of the unit cell. It had been generally thought during the early stages of research on this material that the transition from orthorhombic to tetragonal occurs near an oxygen stoichiometry of $x = 6.5$, where the average valence of copper is two. However, despite numerous studies of this system, the transition from an orthorhombic to a tetragonal structure has not been rigorously defined. For example, by employing a zirconium gettering technique, Cava *et al.*[2] studied the oxygen dependence of T_c, resistivity, magnetization, and lattice parameters in $YBa_2Cu_3O_x$ samples below 520°C and found that the orthorhombic structure was retained over a wide composition range $6.3 \leq x \leq 7.0$. It should be noted that for $x = 6.0$, the formal oxidation state of copper is 1.67; at $x = 7.0$, the formal oxidation state is 2.33.

Of particular importance, two pronounced plateaus of T_c versus oxygen content have been obtained within the orthorhombic structure by various investigations, one at $T_c \sim 60$ K ($x \cong 6.6$–6.7), the other at ~ 90 K ($x \cong 6.8$–7.0) joined by a steeply rising line at ~6.7–6.8.[3,4] Cava *et al.*[2] suggest that an ordered oxygen-vacancy phase exists near $x \sim 6.67$. It should be noted that, based on electron diffraction studies,[3,4] the two plateaus of T_c versus x have been associated with oxygen-vacancy ordering and the possible existence of a miscibility gap. However, based on early X-ray diffraction data,[2] the two plateau compositions were single phase, with orthorhombic symmetry over the whole range of compositions.

Two less well defined plateaus are also found, when Nd or Gd are substituted for Y. In addition, as the ion size increases, the orthorhombic structure becomes less stable.[6]

The objective of our studies at Argonne National Laboratory (ANL) is to investigate the structural transformations and thermodynamic behavior of the $YBa_2Cu_3O_x$ and the related systems, $NdBa_2Cu_3O_x$, $GdBa_2Cu_3O_x$, as a function of oxygen partial pressure, oxygen stoichiometry, and temperature by means of a coulometric titration technique where the oxygen content can be varied by well-defined small amounts. The objective of lower temperature measurements is to determine whether the structural changes indicated by the models and calculations of Curtiss *et al.*,[7] Khachaturyan *et al.*,[8] and Wille *et al.*,[9] as well as the experimental studies described above, could be confirmed via EMF measurements carried out at a relatively low temperature.

This paper will review and update the results of our previously reported measurements[10,11,12] on the $YBa_2Cu_3O_x$ system and report on our recent results on the $NdBa_2Cu_3O_x$ system. The results of limited measurements on the n-type (electron-doped) superconducting $Nd_{1.81}Ce_{0.19}CuO_x$ system will also be presented.

EXPERIMENTAL

The electrochemical cell can be schematically represented by

$$\mathrm{Pt,\ M\ (p(O_2))\ |\ ZrO_2(Y_2O_3)\ |\ Air\ (p(O_2) = 0.21\ atm),\ Pt}$$

where M = $YBa_2Cu_3O_x$, $NdBa_2Cu_3O_x$, and $Nd_{1.81}Ce_{0.19}CuO_x$. The equilibrium oxygen partial pressure $p(O_2)$ above the sample in the cell can be calculated by means of the Nernst equation

$$p(O_2) = p(O_2)_{ref}\ exp\ \left(-\frac{4EF}{RT}\right)$$

where E is the EMF (open circuit potential) of the cell, F is the Faraday constant, T is the absolute temperature and R the gas constant.

The oxygen content of the sample under investigation can be varied by means of coulometric titration and calculated from the relationship

$$\Delta n(O_2) = \frac{It}{4F}$$

where $\Delta n(O_2)$ = moles of oxygen transported, I is the controlled current (amps) flowing through the cell for a time t (sec), and F is the Faraday constant. It should be noted that yttria-stabilized zirconia has a high mobility of oxygen ions in the lattice of the electrolyte.

The cell used in this study was based on the cell designs described by Tretyakov and Rapp,[13] except that soft glass was used as a sealant instead of Pyrex. Pure air circulating over the cell served as the reference electrode. The cell EMF was measured with a high-impedance electrometer and a Keithley digital voltmeter. Coulometric titrations were performed with a Princeton Applied Research Model 173 Potentiostat/Galvanostat. The stabilized zirconia electrolyte served as both an oxygen pump and a sensor for EMF measurements. The samples used for EMF measurements were prepared by the Materials Science Division at the Argonne National Laboratory. The $YBa_2Cu_3O_x$ sample was received in the form of a ten mil thick sintered tape (~95% theoretical density). The transition temperature was reported to be ~90 K.[14] X-ray examination showed only the orthorhombic structure; oxygen analysis (iodometric titration) gave $x = 6.891 \pm 0.005$. The tape was broken up into small granules (sample size, ~30 mg) for use in the EMF measurements.

The $NdBa_2Cu_3O_x$ sample was received in the form of a coarse powder. The transition temperature was reported to be ~96 K.[15] X-ray examination showed only the orthorhombic structure; oxygen analysis via iodometric titration gave 6.910±0.005. The composition of the as-received n-type sample (coarse powder) was $Nd_{1.81}Ce_{0.19}CuO_4$. X-ray analysis showed essentially the tetragonal structure and a minor cubic phase estimated to be $Ce_{0.5}Nd_{0.5}O_{1.75}$. The transition temperature was reported to be ~24 K.[16]

It should be emphasized that the advantage of the EMF technique compared to thermogravimetric analyses (TGA) is that very small samples (~25–30 mg) can be studied, and the composition of the condensed phase varied by small incremental amounts. In the case of TGA, 1 gram samples are generally used; however, problems due to convectional gas flow and thermal drift can reduce the sensitivity of the TGA technique.

RESULTS AND DISCUSSION

Y-Ba-Cu-O System

The essential highlights of our previously published results on the $YBa_2Cu_3O_x$ system are summarized below.

The results of our EMF measurements are shown in Fig. 1 where equilibrium oxygen pressures calculated for isotherms in the temperature range 400-750°C are plotted as a function of x in $YBa_2Cu_3O_x$. No apparent sign of a change in curvature at an oxygen stoichiometry of x ~6.5 where the formal valence of copper is two, and where the O-T transition had been assumed to occur by various investigators during the early stages of research on this material. Based on X-ray analyses of several samples, our results show that the O-T transition occurs at an oxygen stoichiometry of $x \leq 6.4$. It should be emphasized, however, that the oxygen stoichiometry at which the O-T structural transition occurs depends on the annealing temperature and time and partial pressure of oxygen above the material under investigation.

Of particular importance, the change in curvature of the lower temperature isotherms above $x = 6.5$ shown in Fig. 1 and an inflection around $x = 6.65$ are consistent with the presence of a miscibility gap at lower temperatures. Based on a linear fit, and the thermodynamic relationship $\frac{d\,log\,p(O_2)}{d(\frac{1}{T})}$, our values of log $p(O_2)$ versus x, when extrapolated to temperatures below 400°C , indicated the presence of a miscibility gap. From the shape of the extrapolated isotherms we estimated that the miscibility gap lies below a consolute temperature of ~ 200±50 °C. For the terminal compositions extending between $x = 6.55$ to $x = 6.75$ we estimated a temperature of ~35°C.

In addition, a relatively rapid increase of the partial molar entropy of solution of oxygen in $YBa_2Cu_3O_x$ in the composition range $x \cong 6.75\text{-}6.55$ appears to reflect the properties of an orthorhombic-orthorhombic miscibility gap since the extrapolated measurements appear to be completely within the orthorhombic phase field. The increase in $\Delta\overline{S}(O_2)$ with oxygen deficiency in $YBa_2Cu_3O_x$ at x <6.5 is related to the O-T transition and reflects the differences between the distributions of oxygen atoms and vacancies in the relatively disordered tetragonal structure and the more ordered orthorhombic structure. The trend in the values of $\Delta\overline{S}(O_2)$ as well as their absolute values have been confirmed by the recent results of Meuffels *et al.*[17] In this work, p-x isotherms were measured by means of a computer-controlled volumetric system in which desorption-absorption experiments were carried out. The results of Meuffels et al. also show that partial molar entropy values exhibit large negative deviations from ideal solution behavior, particularly in the composition range reflecting the orthorhombic structure. In agreement with our results, the results of Meuffels et al., show that the partial molar enthalpy of oxygen in YBa_2Cu_3Ox depends weakly on oxygen stoichiometry. Figures 3 and 4 show a comparison of these partial molar quantities obtained by Meuffels et al., and those derived from our EMF measurements.

The results of our assessment of $\Delta\overline{S}(O_2)$ and $\Delta\overline{H}(O_2)$ values based on our analyses of TGA measurements reported by various investigations was summarized in a previous paper.[12] Briefly, over the composition range 6.2-6.8, the results of our EMF measurements are in general agreement with the $\Delta\overline{S}(O_2)$ values which we calculated from the measurements of Strobel et al.[18], Specht et al.[19], Lindemer et al.[20] and Yamaguchi et al.[21] However, the $\Delta\overline{S}(O_2)$ values estimated from the TGA measurements of Kishio et al.[22] and Gallagher et al.[23] are in poor agreement with the results derived from our EMF measurements. Our $\Delta\overline{H}(O_2)$ are in rough agreement with the values derived from the TGA measurements of Strobel et al., Specht et al (except at x=6.2), Lindemer et al. and Yamaguchi et al. However, the partial molar enthalpy values derived from TGA measurements of Kishio et al. and Gallagher et al., are in poor agreement with the bulk of the above values. The results of our assessments of partial molar quantities, $\Delta\overline{S}(O_2)$ and $\Delta\overline{H}(O_2)$, are shown in Figures 4 and 5. Included in Figures 4 and 5 are $\Delta\overline{S}(O_2)$ and $\Delta\overline{H}(O_2)$ values based on our assessment of p-x TGA isotherms of Marucco et al.[24]

The presence of a miscibility gap at low temperatures due to two orthorhombic structures has been suggested by a number of theoretical studies. Curtiss *et al.*[7] postulated a phase diagram based, in part, on semiempirical molecular orbital theory, which suggested two orthorhombic structures in the region x >6.5. They speculated that one of the structures would have fully occupied oxygen chain sites (01), while the other would have partially occupied chain sites. Khachaturyan *et al.*[8] estimated a phase diagram based on a mean field model and experimental data for the T→O transition. Their calculated diagram predicts a peritectoid decomposition into two phase fields below ~190°C, namely, O' (where x =6.5) + O_x, or O' + T. Wille *et al.*[9] have calculated a phase diagram by application of the cluster variation method to an asymmetric two-dimensional Ising model with interaction parameters selected to guarantee the stability at x =6.5 of the experimentally observed double cell structure. Their calculated phase diagram shows a miscibility gap having two orthorhombic structures. Goodenough and Manthiram[25] have also suggested that interchain ordering of the oxygens can give rise to several discrete Magneli-type orthorhombic structures.

From the more recent results of Khachaturyan et al.[8], de Fontaine et al.[9], and Hyland et al.[26], we conclude that at a stoichiometry of x=6.5, a coulombically ordered structure exists at low temperature with oxygens in the basal planes forming alternating planes of chains of divalent oxygen and vacancies. As more oxygen is added, pairs of oxygen planes form some oxygen plane pairs which alternate with vacancy planes to form a Magneli series. At the idealized stoichiometry of x=7.0, oxygen replace all of the vacancies. It appears that the valence of copper remains at 2 at x>6.5 and that beyond this stoichiometry, some of the oxygens (x=7.0) in the basal plane are monovalent. Therefore, compositions between 6.5 and 7.0 can be thought of as being formed by mixing O^{2-} - vacancy pairs (which have net dipoles) with O^{-}–O^{-} pairs (which have a no net charge in the solid). Mixing of dipole "ion" pairs with a neutral solvent will generally be accompanied by a positive energy change and large positive deviations from ideality if the effective dielectric constant of the neutral solvent is not very large. Such a phenomenon would be accompanied by strong association of the ion pairs (O^{2-}–vacancy pairs in this case) with small stoichiometric numbers of species per mole of divalent oxygen plus vacancies governing the limiting laws of the solution. Preliminary examination of our results at high values of x indicates a small stoichiometric number, and that the presence of O^{2-}– vacancy pairs or larger clusters is consistent with our data. Further analyses of the data are in progress.

Of importance, the recent results of Veal et al.[27] show that the superconducting properties of $YBa_2Cu_3O_{6.45}$ quenched from 520°C in liquid N_2 are found to be time dependent when annealed at room temperature following the liquid nitrogen quench. The T_c increased as much as 15 K in a period of several days after annealing at room temperature with no apparent change in oxygen stoichiometry. According to Veal et al, oxygen atoms at the O5 sites move to neighboring O1 sites resulting in oxygen-vacancy ordering. However, based on the the results of neutron diffraction measurements, Jorgensen et al.[28] attribute the increase in T_c to local ordering of oxygen atoms around the Cu1 atoms with no change in the average site occupancy; the dominant effect is a shortening of the c axis that results from charge transfer between the chains and planes.

Nd-Ba-Cu-O System

In agreement with the results obtained with the $YBa_2Cu_3O_x$ system, no apparent change in curvature or discontinuity was observed at an oxygen stoichiometry of $x = 6.5$ where copper is divalent and where the orthorhombic-tetragonal transition had been assumed to occur. The results of our EMF measurements are shown in Figure 6, where equilibrium oxygen pressure calculated for isotherms in the temperature range 400–600°C are plotted as a function of x in $NdBa_2Cu_3O_x$.

It should be emphasized that coulometric titrations yield the change in stoichiometry δx from a given composition, x, in $NdBa_2Cu_3O_x$. The reference composition after our cell was sealed and EMFs measured prior to coulometric titrations was based on the data of Kishio et al.[29], and corresponded to a value of x = 6.56_5.

The shape of the 400°C isotherm shown in Figure 3 for $NdBa_2Cu_3O_x$, although not as pronounced as with the $YBa_2Cu_3O_x$ system, suggests the presence of a miscibility gap at lower temperatures, at values of x that are higher than those in the $YBa_2Cu_3O_x$ system. It should be noted that the location of the miscibility gap is consistent with the observed composition dependence of T_c for $YBa_2Cu_3O_x$ and $NdBa_2Cu_3O_x$ systems. The results of Veal et al.[30] show that with increasing ionic radius in the sequence Y, Gd, Nd, the falloff of T_c increases with oxygen deficiency. Also, the oxygen stoichiometry where superconductivity is lost increases with increasing ionic radius. In addition, their results show that the lower plateau is nearly absent for the case of $NdBa_2Cu_3O_x$. Ionic radii of trivalent Y, Gd, and Nd (reported in their paper) are 0.99 , 1.02, and 1.10 angstroms respectively. According to Shaked et al.[31], the repulsion energy of oxygen atoms in O1 and O5 lattice sites in $NdBa_2Cu_3O_x$ is smaller than in $YBa_2Cu_3O_x$. The lower repulsion energy stabilizes the orthorhombic structure at higher values of x in $NdBa_2Cu_3O_x$ compared to $YBa_2Cu_3O_x$.

Some hysteresis was observed at 400°C during desorption of oxygen from $NdBa_2Cu_3O_x$ when x had reached a value of $\sim$6.9. The oxygen stoichiometry was reduced to a value of $x \sim 6.35$ and then increased again via coulometric titration. Unfortunately, after reaching a value of $x \cong 6.6$, a power failure occurred, resulting in rapid cooling of the furnace, and failure of the cell due to a leak. The results are shown in Figure 7. Additional experiments will be performed in order to establish whether the hysteresis observed at 400°C is real.

Our results obtained with the $NdBa_2Cu_3O_x$ system show that at a given stoichiometry, partial pressures of oxygen are higher than for the $YBa_2Cu_3O_x$ system, in accord with calculated partial thermodynamic quantities. Typical results at 500°C are shown in Fig.8, and intercomparison of partial thermodynamic quantities calculated from our EMF measurements on these systems are given in Table I.

We are currently collecting EMF data on the $GdBa_2Cu_3O_x$ system. The results of these measurements will be reported in a later paper.

Nd-Ce-Cu-O System

Preliminary EMF measurements as a function of oxygen stoichiometry were made on the n-type (electron -doped) superconductor $Nd_{1.81}Ce_{0.19}CuO_x$ (T_c=24 K, x =4).[32] X-ray examination of the starting material showed the expected tetragonal structure and also a minor cubic phase $Ce_{0.5}Nd_{0.5}O_{1.75}$. Reducing the oxygen partial pressure via coulometric titration at 750°C resulted in an oxygen partial pressure plateau, $p(O_2) = 3.2 \times 10^{-4}$ atm, over a narrow composition range, $x = 3.97_5 - 3.96_6$, indicating a diphasic region. Reversibility was not achieved during oxygen uptake, and the run was terminated when the oxygen stoichiometry reached a value of $x = 3.97_5$, $p(O_2) = 0.25$ atm. The results are shown in Fig. 9. X-ray analyses of the residue after furnace cooling to room temperature did not reveal decomposition of the sample, namely, Nd_2O_3, CeO_2, and Cu_2O were not detected as minor phases; the residue was identical to the starting material. However the transition temperature was found to be 13 K.[16] Additional runs are planned over a wide range of temperatures and composition. It is apparent from the results shown in Figure 9 that the oxygen nonstoichiometry obtained by Suzuki et al.[33] via TGA measurements with $Nd_{1.85}Ce_{0.15}CuO_{4-\delta}$ at 750°C is much smaller, namely, δ=0.002, than that obtained via our EMF measurements. It should be noted that the results of recent extensive studies of Jorgensen et al.[34] on the $Nd_{2-x}Ce_xCuO_4$ system show that when samples were carefully examined by pulsed neutron and high resolution X-ray diffraction, single phase was formed only with the undoped compound Nd_2CuO_4 and for the optimum superconducting composition x=0.165. All other samples were found to be mixtures of this superconducting composition and non-superconducting material of other compositions. Clearly, further processing and structural studies are required in order to characterize these intriguing n-type (electron doped) class of superconducting materials.

SUMMARY

EMF measurements of oxygen fugacities as a function of oxygen stoichiometry in $YBa_2Cu_3O_x$ and $NdBa_2Cu_3O_x$ have been made in the temperature range 400-750°C by means of an oxygen titration technique with a yttria stabilized zirconia electrolyte. From plots of equilibrium oxygen pressures versus x, no sign of a change in curvature was obtained at an oxygen stoichiometry of $x = 6.5$, where copper is divalent, and where the orthorhombic-tetragonal structural transition had been thought to occur. Of importance, the "S" shape of the 400°C isotherm obtained with $NdBa_2Cu_3O_x$, although not as pronounced as with the $YBa_2Cu_3O_x$ system, suggests the presence of a miscibility gap at lower temperatures at values of x that are higher than those in the $YBa_2Cu_3O_x$ system. The shifts in the location of the miscibility gaps are consistent with the composition dependence of T_c with ionic radii for Y and Nd in $YBa_2Cu_3O_x$ and $NdBa_2Cu_3O_x$. For a given oxygen stoichiometry, partial pressures above $NdBa_2Cu_3O_x$ were found to be higher than that for $YBa_2Cu_3O_x$ in accord with calculated partial molar quantities, $\Delta\overline{S}(O_2)$ and $\Delta\overline{H}(O_2)$. Our results to date appears to explain the two plateaus in measured values of T_c as a function of oxygen stoichiometry in orthorhombic $YBa_2Cu_3O_x$, and appears to be consistent with the less pronounced T_c plateaus found for the $NdBa_2Cu_3O_x$ system at higher oxygen stoichiometry values. Our results indicate that the orthorhombic-orthorhombic and orthorhombic-tetragonal structural transitions are associated with order-disorder second order transitions in the basal plane of $YBa_2Cu_3O_x$ and $NdBa_2Cu_3O_x$ compounds.

The irreversible behaviour of the n-type Nd-Ce-Cu-O system requires further study. Thermodynamic and structural studies during various stages of reduction and oxidation of $Nd_{2-x}Ce_xCuO_4$ are needed to define the nonstoichiometric behaviour of this system.

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Table 1. Comparison of Partial Molar Quantities for $NdBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$ Systems

	$NdBa_2Cu_3O_x$		$YBa_2Cu_3O_x$	
x	$\Delta\overline{H}(O_2)$	$\Delta\overline{S}(O_2)$	$\Delta\overline{H}(O_2)$	$\Delta\overline{S}(O_2)$
6.4	−37.0	−31.4	−38.3	−32.0
6.5	−35.3	−33.0	−37.6	−33.6
6.6	−34.5	−34.6	−36.4	−36.0
6.7	−33.5	−32.8	−38.9	−40.0
6.8	−31.0	−33.6	−37.1	−41.7
6.85	−29.2	−32.3	−37.4	−43.7

$\Delta\overline{H}(O_2)$ values in kcal/mol
$\Delta\overline{S}(O_2)$ values in cal/mol K

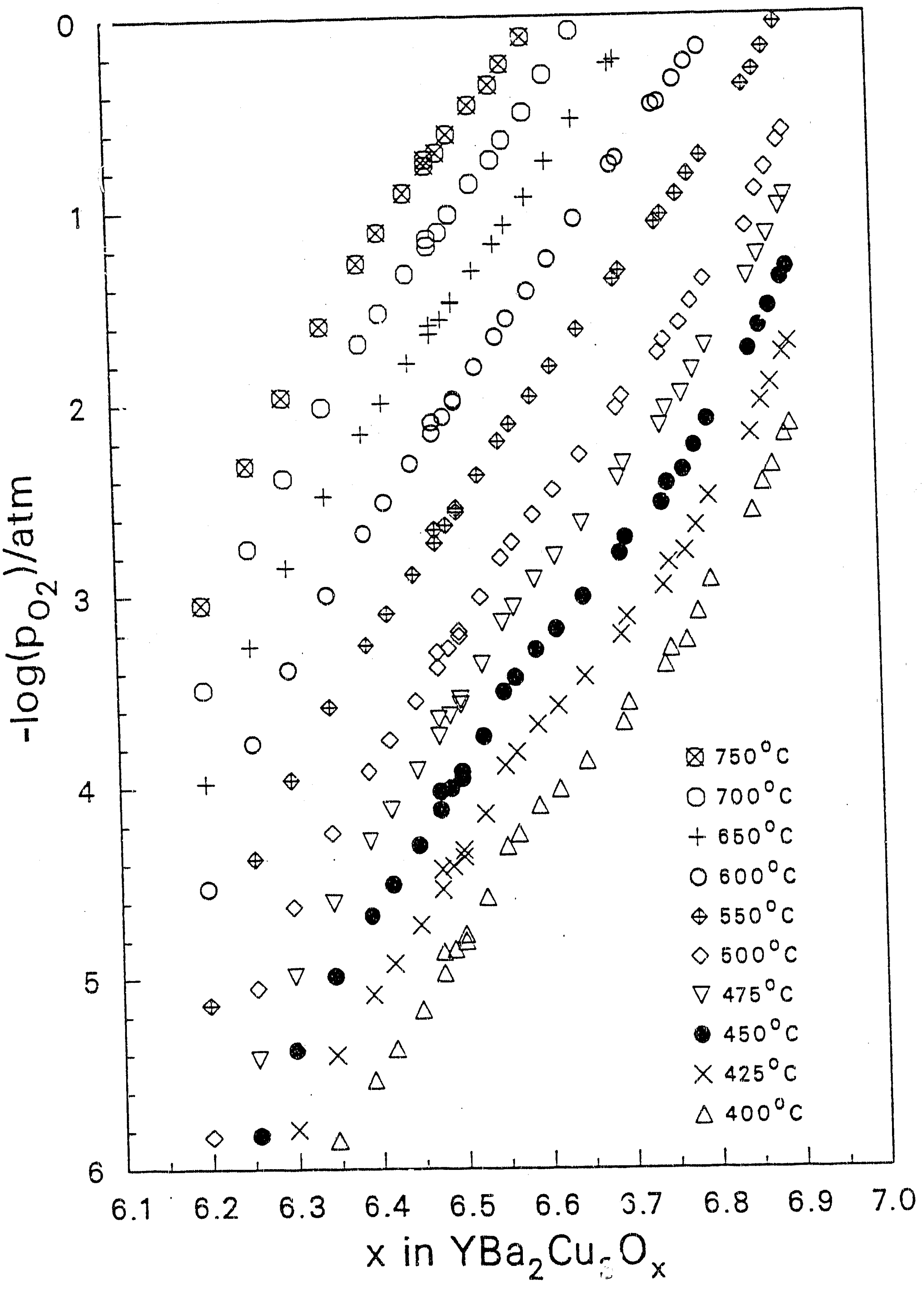

Fig. 1. Partial pressure (fugacity) of oxygen as a function of temperature and oxygen stoichiometry in $YBa_2Cu_3O_x$.

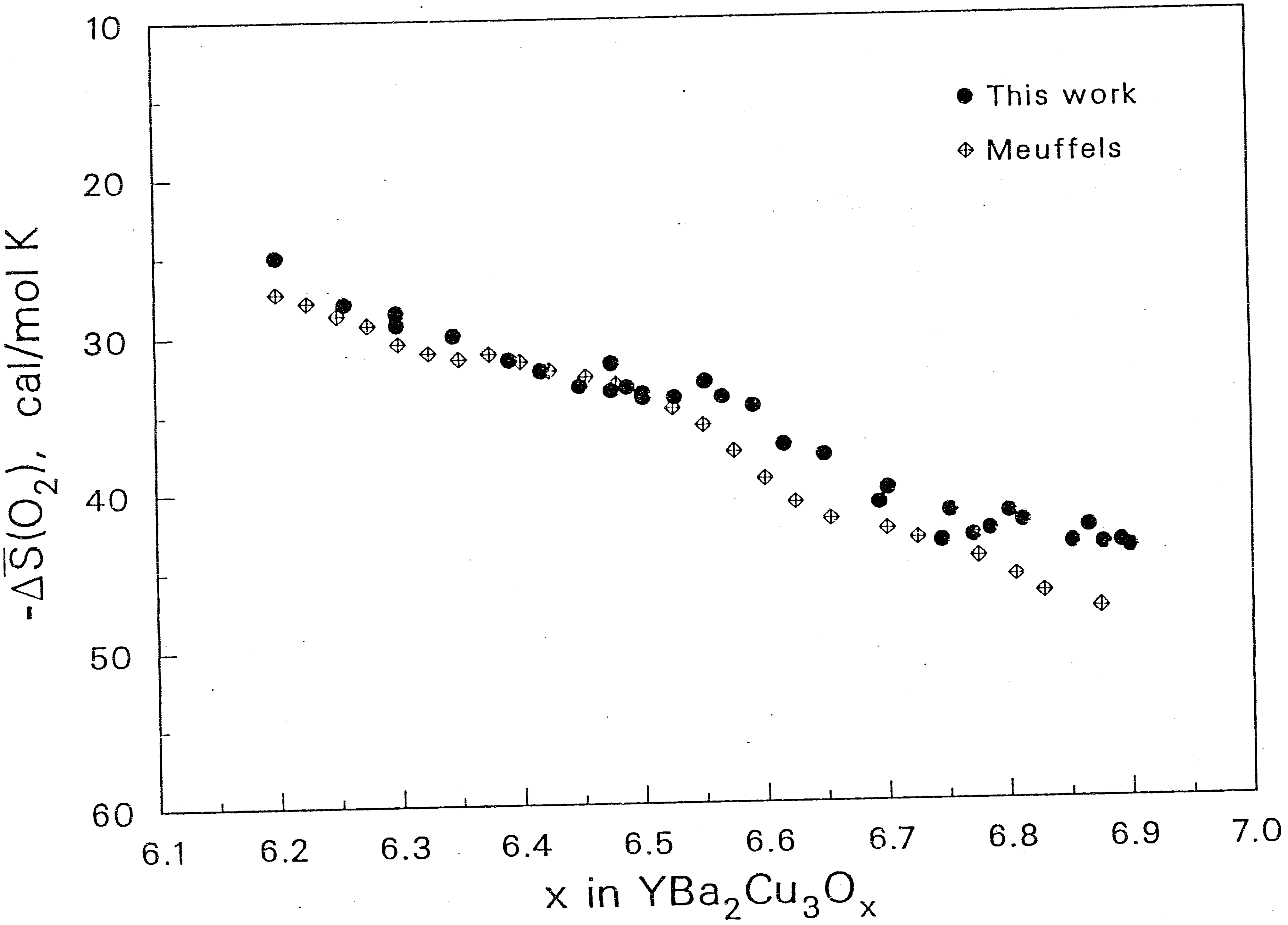

Fig. 2. Comparison of $\Delta S(O_2)$ values in $YBa_2Cu_3O_x$ derived from EMF measurements and recent oxygen sorption measurements of Meuffels.[17]

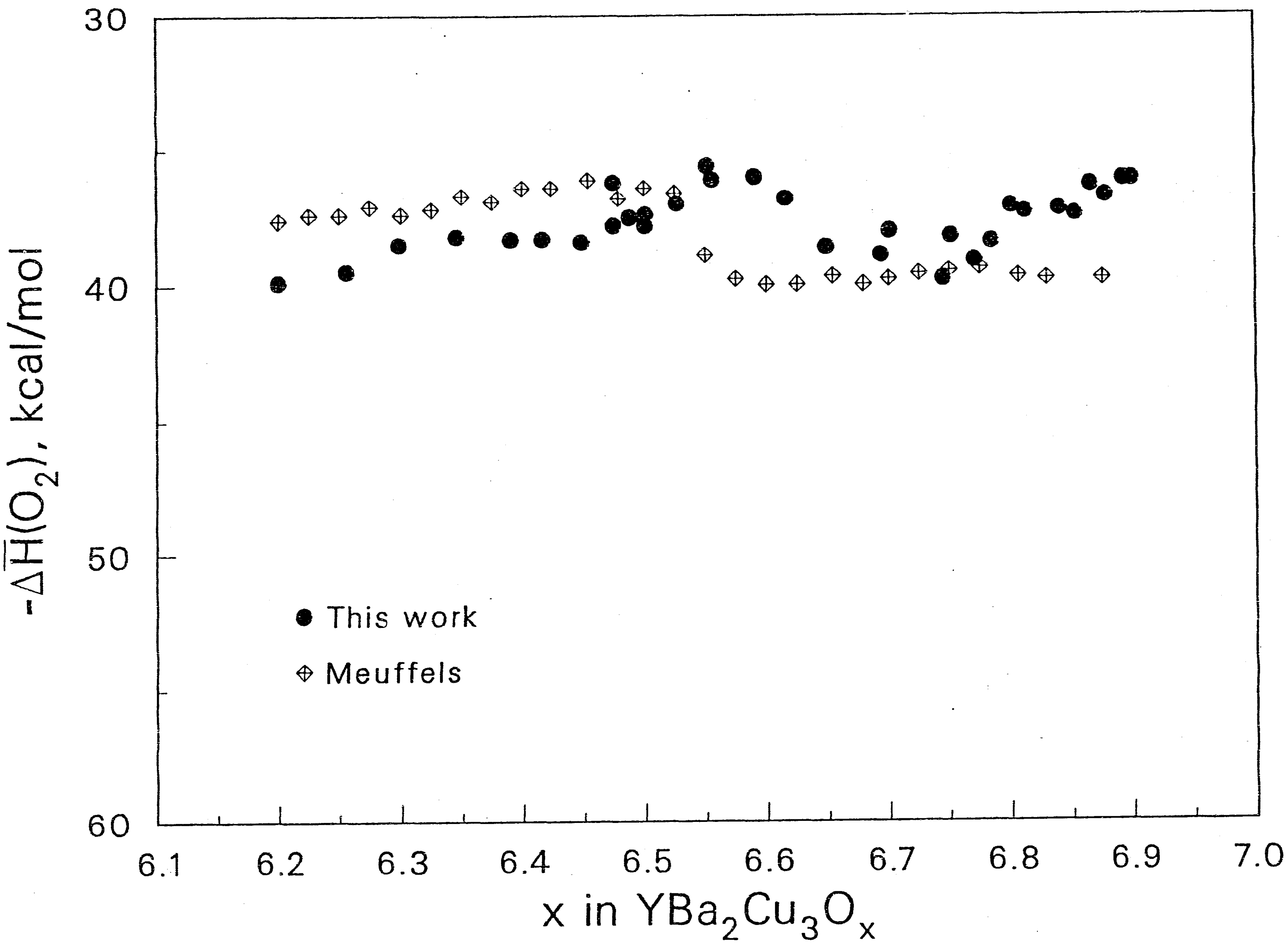

Fig. 3. Comparision of $\Delta H(O_2)$ values in $YBa_2Cu_3O_x$ derived from EMF measurements and recent oxygen sorption measurements of Meuffels.[17]

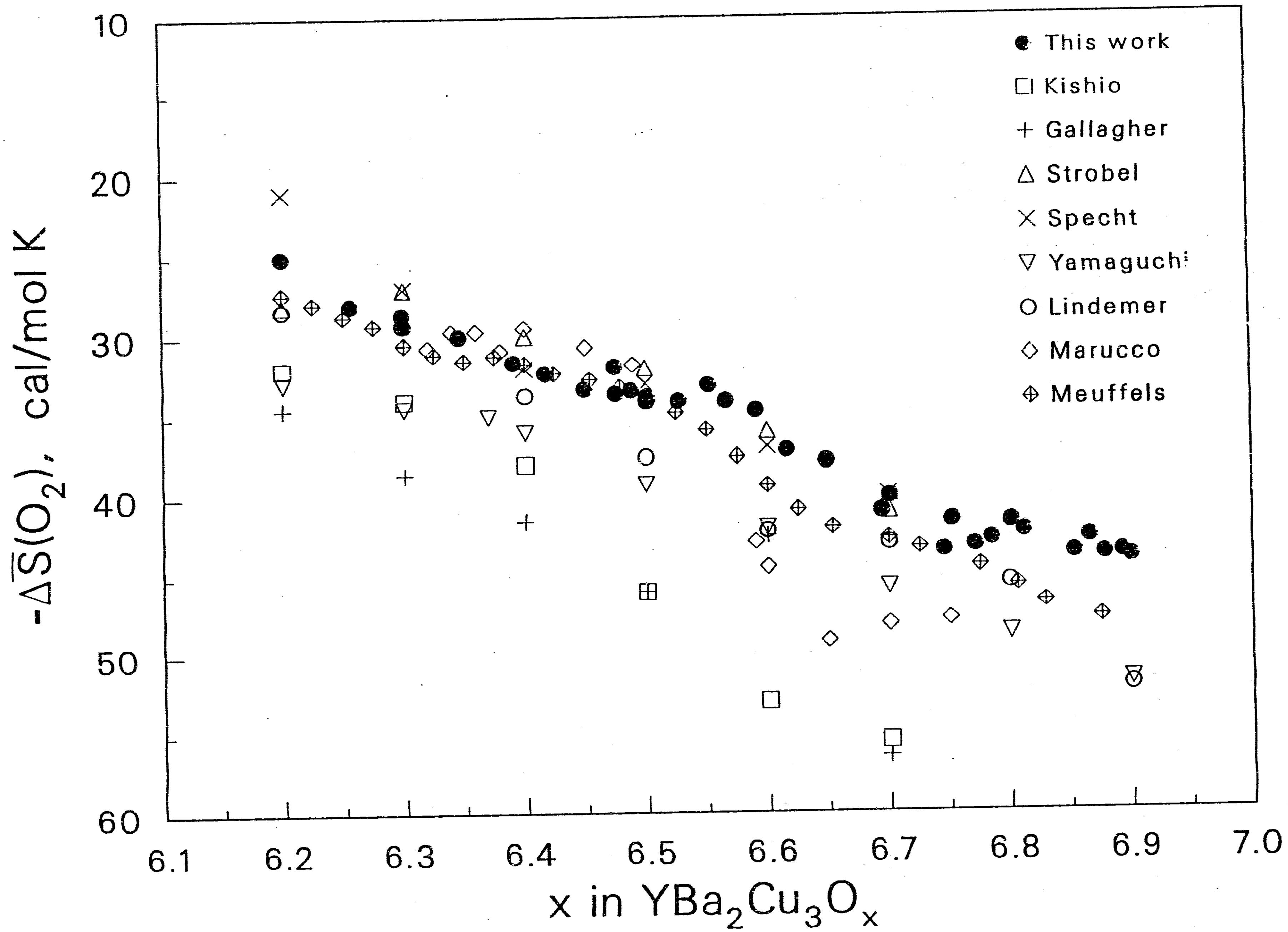

Fig. 4. Comparison of $\Delta\overline{S}(O_2)$ values in $YBa_2Cu_3O_x$ based on our assessment of the results of TGA measurements of various investigations.[18–24]

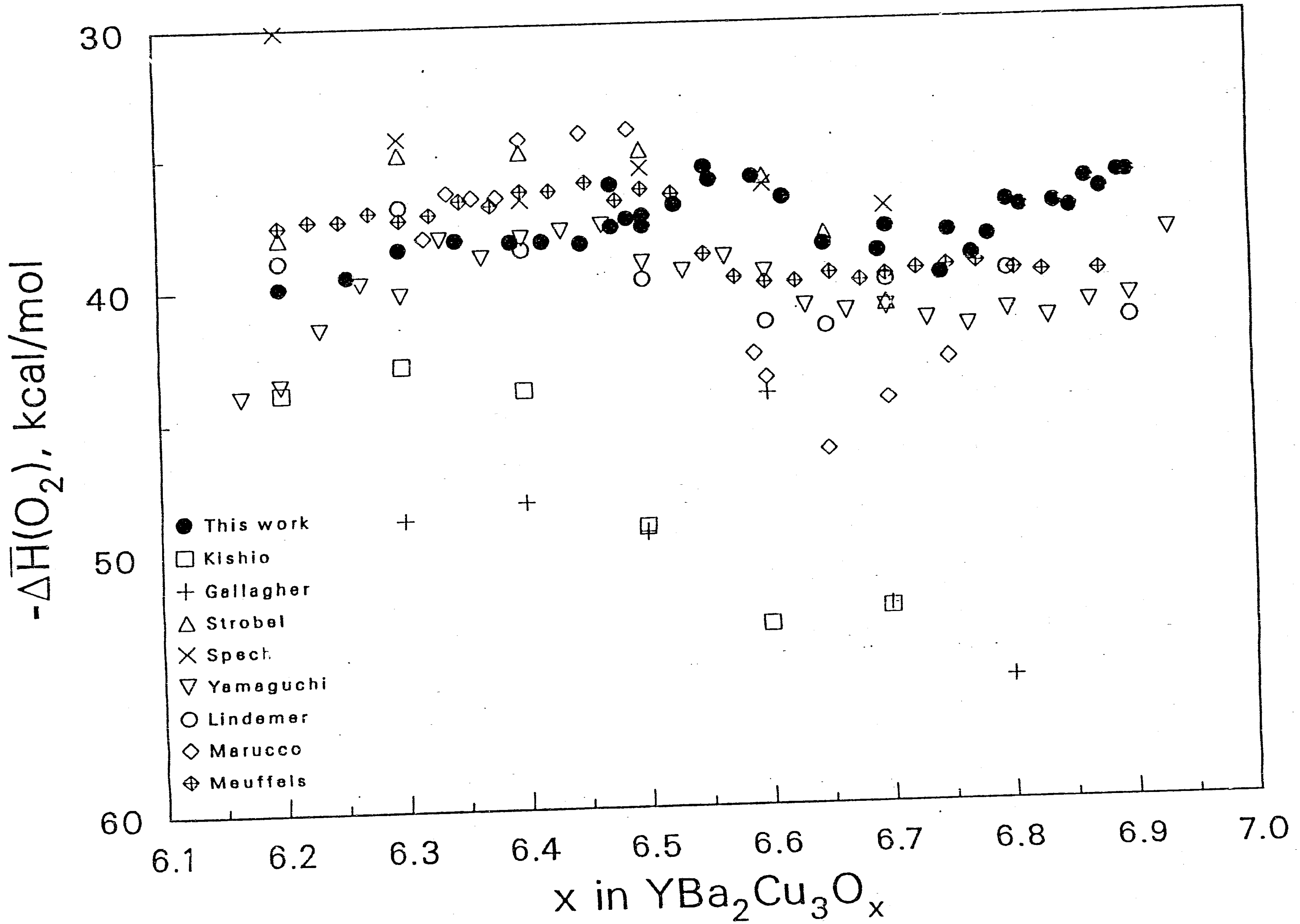

Fig. 5. Comparison of $\Delta\overline{\mathrm{H}}(\mathrm{O}_2)$ values in $\mathrm{YBa_2Cu_3O}_x$ based on our assessment of the results of TGA measurements of various investigations.[18–24]

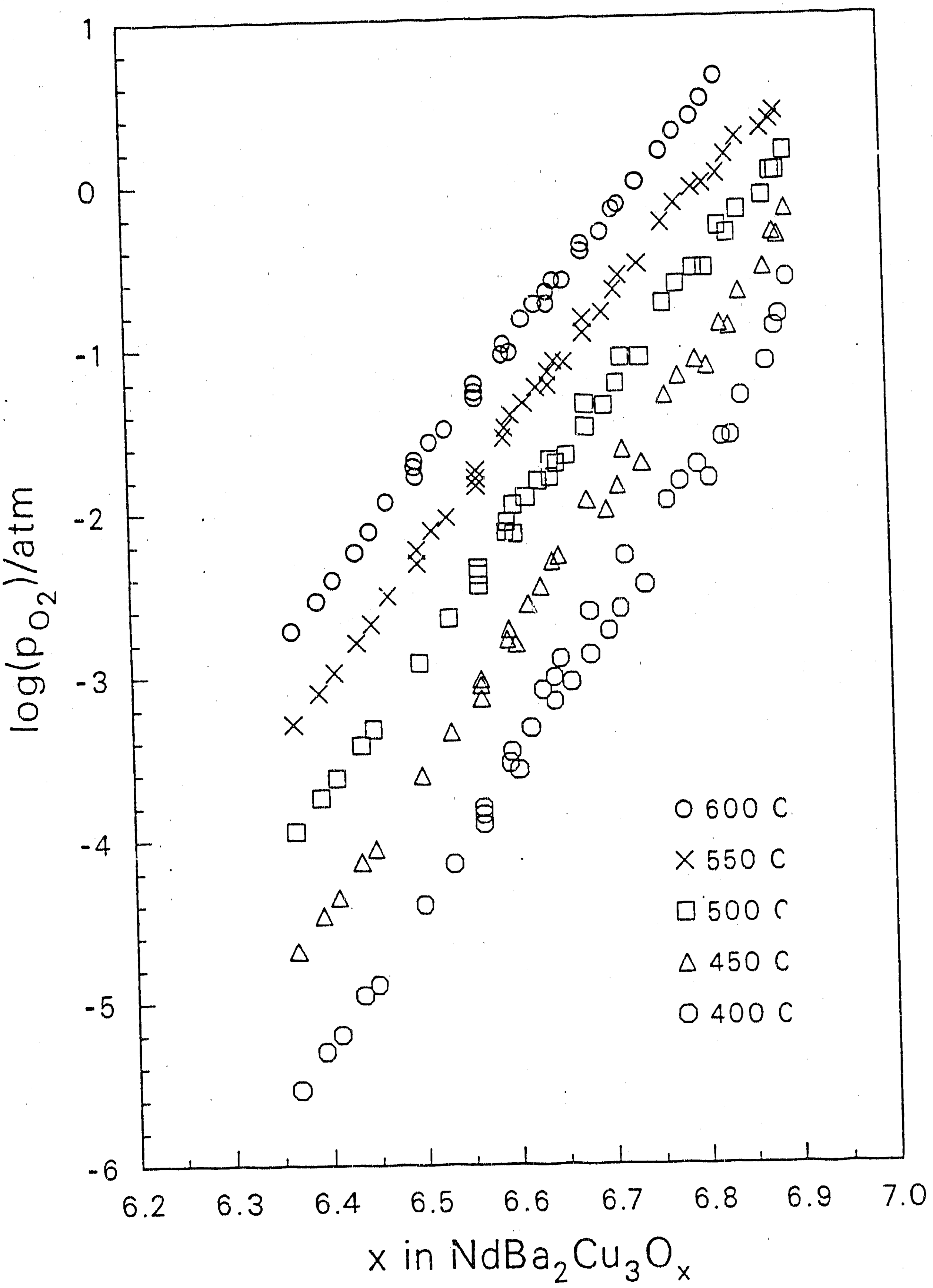

Fig. 6. Partial pressure (fugacity) of oxygen as a function of temperature and oxygen stoichiometry in $YBa_2Cu_30_x$.

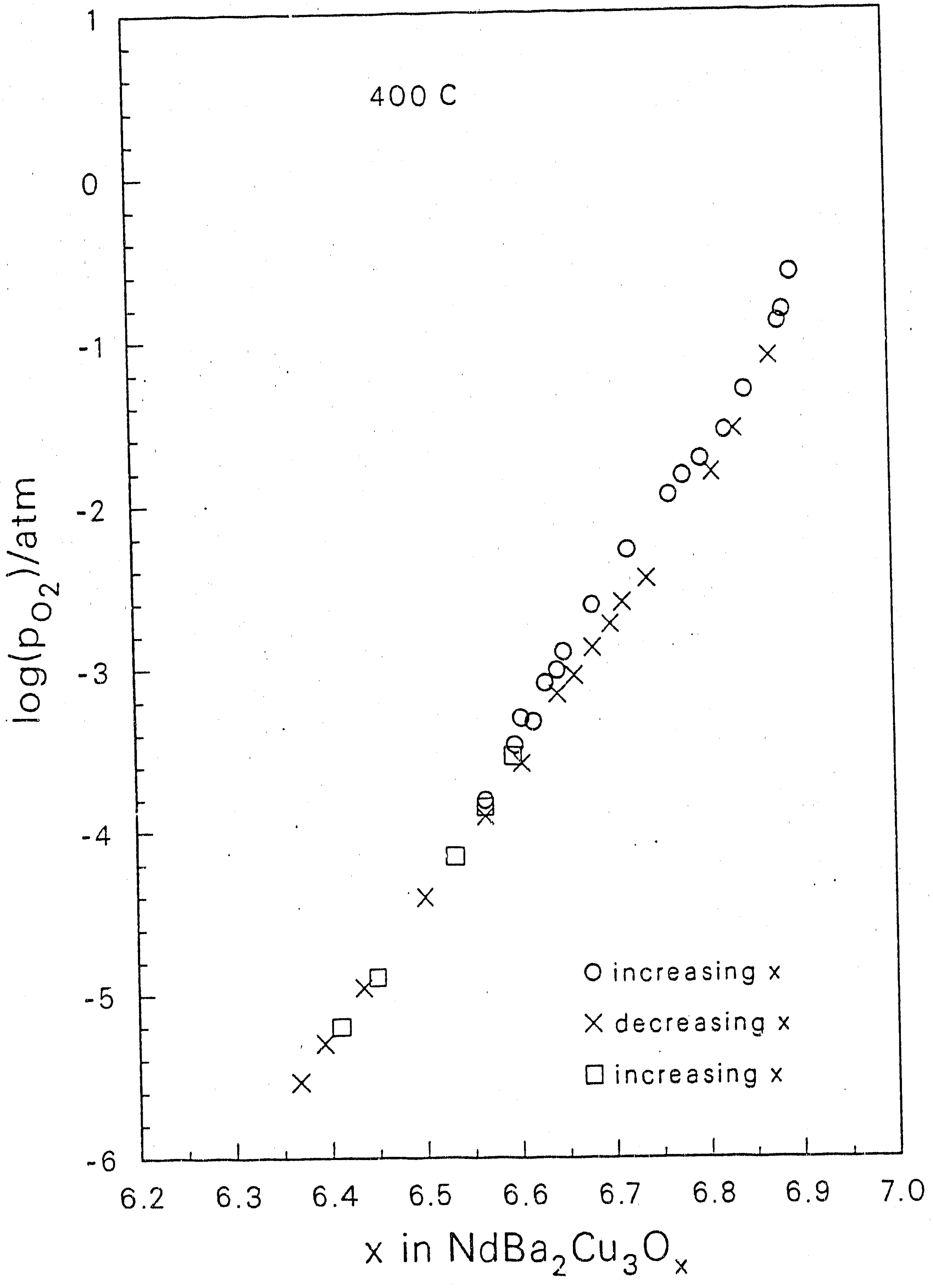

Fig. 7. Partial pressure of oxygen as a function of oxygen stoichiometry in $NdBa_2Cu_3O_x$ at 400°C showing hysteresis.

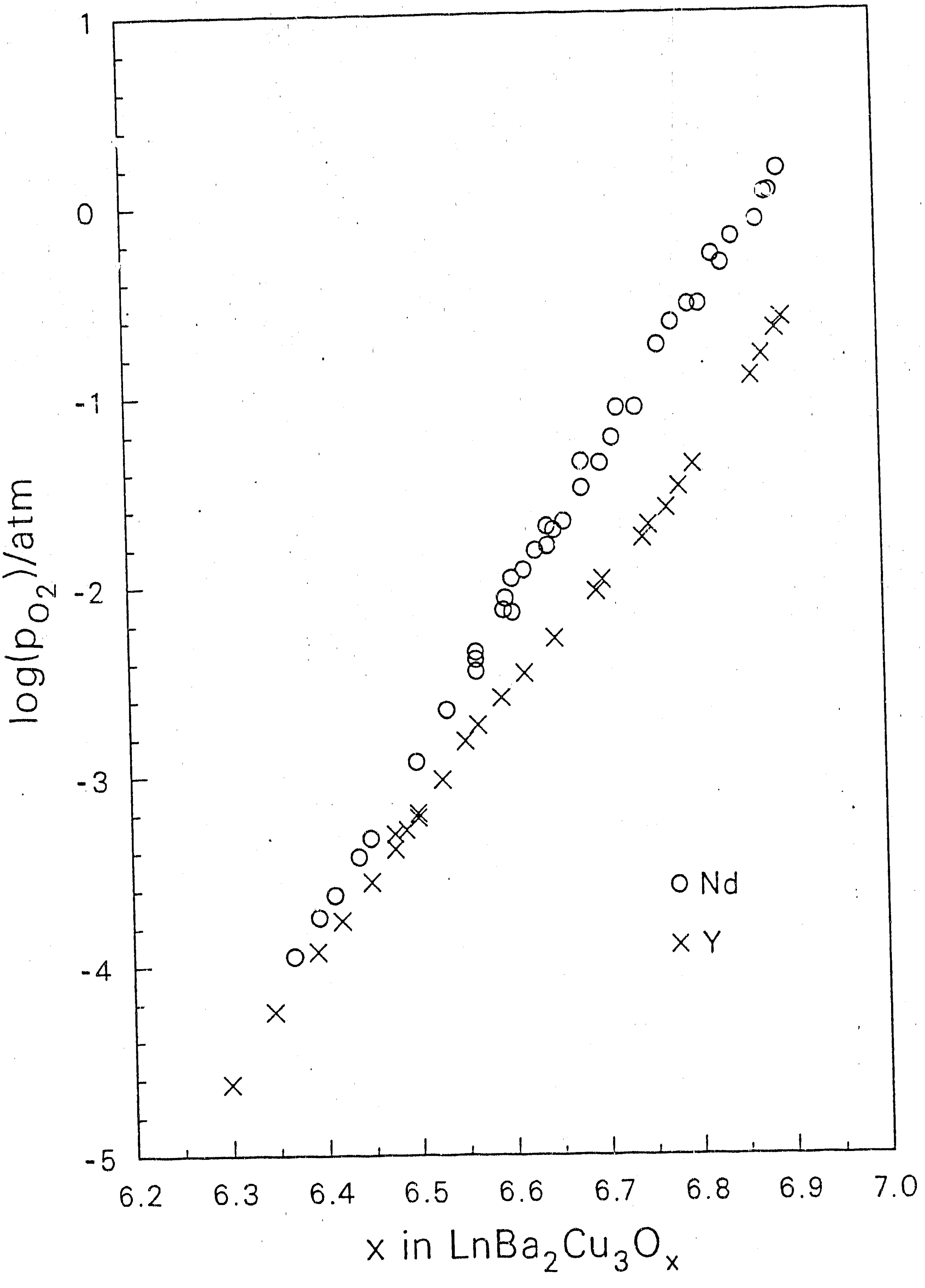

Fig. 8. Comparison of partial pressures above Nd123 and Y123 systems at 500°C.

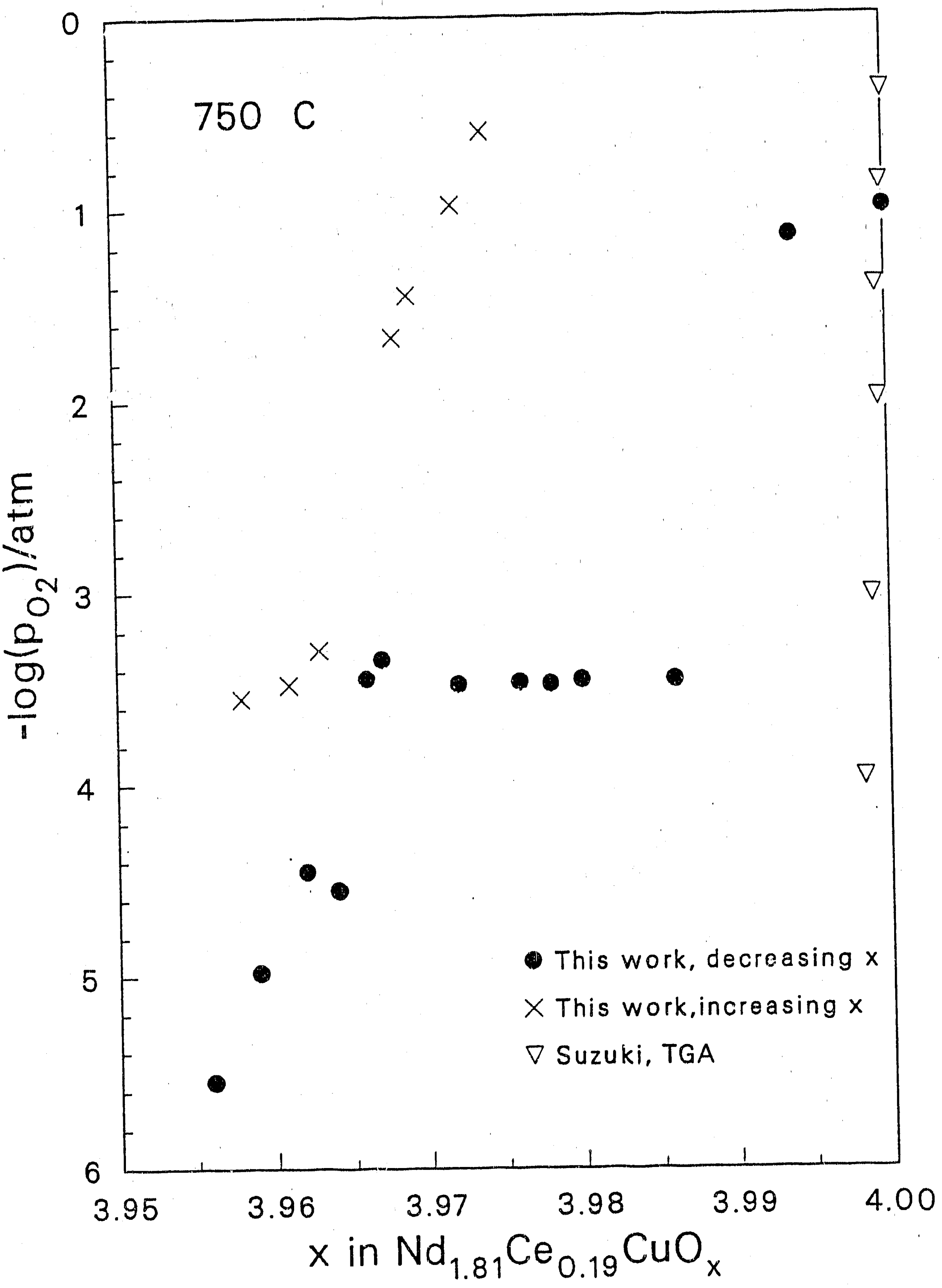

Fig. 9. Partial pressure of oxygen as a function of oxygen stoichiometry in $Nd_{1.51}Ce_{0.19}Cu0_x$ at 750°C. (Suzuki data For $Nd_{1.85}Ce_{0.15}Cu0_x$).[32]

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