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Materials Aspects

12-16 March 1990

Control of Oxygen Deficiency in the Electron Superconductor $Nd_{2-x}Ce_xCuO_{4-y}$ by a Solid State Technique.

M.E. LÓPEZ-MORALES*, B.T. AHN, R.B. BEYERS and P.M. GRANT, IBM Almaden Research Center.-- A necessary condition for superconductivity in the material $Nd_{2-x}Ce_xCuO_{4-y}$ is the removal of oxygen. The way this procedure is done and the amount of oxygen removed is critical for the superconducting properties of the sample. We describe here a method of preparing samples of $Nd_{2-x}Ce_xCuO_{4-y}$ with precisely controlled oxygen content using solid state electrolysis. We find that the physical properties of this system strongly depend on the concentration and ordering of the oxygen atoms. Careful control of these factors lead to samples with superior electronic properties.

*On leave from Instituto de Investigaciones en Materiales, UNAM

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**Supported by U.S. DOE, Basic Energy Sciences-Materials Science under Contract #DE-AC 02-76ER 01198.
[1]S. J. Rothman, J. L. Routbort, and J. E. Baker, to be published in Phys. Rev. B.

11:48
R17 5 Theory of Oxygen Diffusion in Bulk and Twin Boundary of $YBa_2Cu_3O_{7-x}$. J. S. Choi, M. Sarikaya, I. A. Aksay, R. Kikuchi, Univ. of Washington. --Oxygen diffusion coefficients in the $YBa_2Cu_3O_{7-x}$ superconducting compound are calculated by employing the pair approximation of the Path Probability Method. The results show that the oxygen diffusion in this compound is significantly dependent on the oxygen density and the degree of long-range order. It is found that the oxygen diffusion rate in the tetragonal phase is faster than that in the orthorhombic phase, with the activation energies for diffusion of 0.8 and 1.2 eV, respectively, and it changes abruptly when the phase transformation takes place. We discuss the relationship between oxygen diffusion and each pair probability in connection with each pair's interaction energy values. The kinetics of oxygen diffusion from the present model is discussed in the context of experimental values in the literature and with respect to twin boundary diffusion.
*Supported by DARPA/AFOSR through Boeing under contract HB 2121.

12:00
R17 6 The Effect of Reduction and Reoxidation on Superconducting Properties of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$. A. R. MOODENBAUGH, YOUWEN XU, M. SUENAGA, R. L. SABATINI AND YIMEI ZHU, Brookhaven National Lab.* -- Samples of $YBa_2(Cu_{1-x}Fe_x)_3O_{7-\delta}$ are first prepared by a previously described method.1 Next, approximately one formula oxygen is removed by heating in argon at 830°C, then added back by heating in oxygen at 400°C.[2] The resulting reoxidized samples display the orthorhombic structure in xrd[2] (as well as twins in TEM) for x up to at least 0.08, whereas the original specimens show an orthorhombic/-tetragonal phase boundary for x≈0.03. Superconducting transition temperatures (measured magnetically) are several degrees higher in the resulting orthorhombic samples. Preliminary microprobe studies confirm that the Fe does remain in the major phase after all processing steps.
*Supported by the US DOE Office of Basic Energy Sciences, Division of Materials Science, under contract DE-AC02-76CH00016.

1 Youwen Xu, et al., Phys. Rev. B 39, 6667 (1989).
2 S. Katsuyama, et al., Mat. Res. Bull. 24, 603 (1989).

12:12
R17 7 Partial Substitution of Transition Row Elements for Copper in $Bi_2Sr_2CaCu_2O_8$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ - Sample Preparation and X-ray Structure.. P.M. THIBADO, T.E. JONES, R.D. BOSS, W.C. McGINNIS, Naval Ocean Systems Center;* S. OSEROFF, San Diego State University.**--Preparation conditions used to substitute 5 mol % of the first transition row of elements - Ti, V, Mn, Fe, Co, Ni, and Zn for Cu into both $Bi_2Sr_2CaCu_2O_8$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ will be described. All these elements were substituted into the 2212 phase with a minimum of processing. Partial substitution into the 2223 phase (maintaining phase purity) has only been possible for Ti, V, Mn, and Zn by varying the processing temperature (835°C to 860°C). All attempts to produce x-ray single-phase-purity samples of 2223 with Co, Ni, and Fe substitutions for Cu have been unsuccessful. The measured change in the c-axis lattice parameter scales with the ionic radii of the substituent. The maximum c-axis lattice spacing change observed was (-0.06 ±0.01 Å) for Fe^{2+} in 2212, and (-0.07 ±0.01 Å) for V^{3+} in 2223.
* Supported by the NOSC Independent Research Program.
** Supported by NSF under grant NSF-DMR-8801317.

12:24
R17 8 Partial Substitution of Transition Row Elements for Copper in $Bi_2Sr_2CaCu_2O_8$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$ - Superconducting Properties. T.E. JONES, P.M. THIBADO, R.D. BOSS, W.C. McGINNIS, Naval Ocean Systems Center;* S. OSEROFF, San Diego State University.**--The first transition row of elements (Ti, V, Mn, Fe, Co, Ni, and Zn) have been substituted, at 5 mol % for Cu, into both $Bi_2Sr_2CaCu_2O_8$ and $(Bi,Pb)_2Sr_2Ca_2Cu_3O_{10}$. In the 2212 phase, x-ray data suggest that all these elements go into the structure. The effect on T_c is greatest for the Fe and Co substitutions where the T_c (midpoint) is reduced from 82 K to 60 K. For the 2223 phase, all these elements except Fe and Co go into the structure while maintaining single-phase-purity (the Ni only goes in as mixed phase material - 90% 2223 and 10% 2212). The effect on T_c is greatest for the Ni, Zn, and Mn, where the T_c (midpoint) is reduced from 109 K to 92 K, 102 K, and 103 K, respectively. The magnetic moments of the substituent ions in the lattice have also been determined by high temperature ($T > T_c$) magnetic susceptibility.
* Supported by the NOSC Independent Research Program.
** Supported by NSF under grant NSF-DMR-8801317.

12:36
R17 9 Control of Oxygen Deficiency in the Electron Superconductor $Nd_{2-x}Ce_xCuO_{4-y}$ by a Solid State Technique. M.E. LÓPEZ-MORALES*, B.T. AHN, R.B. BEYERS and P.M. GRANT, IBM Almaden Research Center.-- A necessary condition for superconductivity in the material $Nd_{2-x}Ce_xCuO_{4-y}$ is the removal of oxygen. The way this procedure is done and the amount of oxygen removed is critical for the superconducting properties of the sample. We describe here a method of preparing samples of $Nd_{2-x}Ce_xCuO_{4-y}$ with precisely controlled oxygen content using solid state electrolysis. We find that the physical properties of this system strongly depend on the concentration and ordering of the oxygen atoms. Careful control of these factors lead to samples with superior electronic properties.
*On leave from Instituto de Investigaciones en Materiales, UNAM

12:48
R17 10 Bulk Superconductivity at 62K and Transport Properties in Ce-doped $TlSr_2CaCu_2O_7$. B.L. RAMAKRISHNA, Arizona State U.; Z. IQBAL, Allied Signal Inc; T. DUTTA, U. of South Carolina — Using extended firing times at 925 C followed by quenching and Au tubes sealed in O_2, we were successful in doping a Tl-based cuprate with Ce(IV) to form nearly single phase (as judged by x-ray diffraction and electron microprobe analysis) $Tl_{1-x}Ce_xSr_2CaCu_2O_7$. At x=.25, bulk superconductivity determined by field cooled magnetization data together with zero resistance was observed at 62K. Details of the structure were determined by powder x-ray diffraction and lattice imaging. Single phase quenched samples showed metallic resistivity with decreasing temperature whereas slow cooled and multiphase samples showed semiconducting behaviour. Because of the implications of doping of the Tl(III) sites by Ce(IV) Hall measurements on the specimens will be discussed.

13:00
R17 11 **Laser Melt Processing & Growth of Annular Rings of High T_c Superconductors.†** N.K. Jaggi* & A. Amiri-Hezaveh+ **Northeastern University, Boston,* +*MIT, Cambridge, MA* -
Laser float zone crystallization has been known for a while [1]

Control of Oxygen Deficiency in the Electron Superconductor Nd-Ce-Cu-O by a Solid State Ionic Technique.

Maria Eugenia Lopez-Morales,
B.T. Ahn, R. Beyers
and P.M. Grant.

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IBM

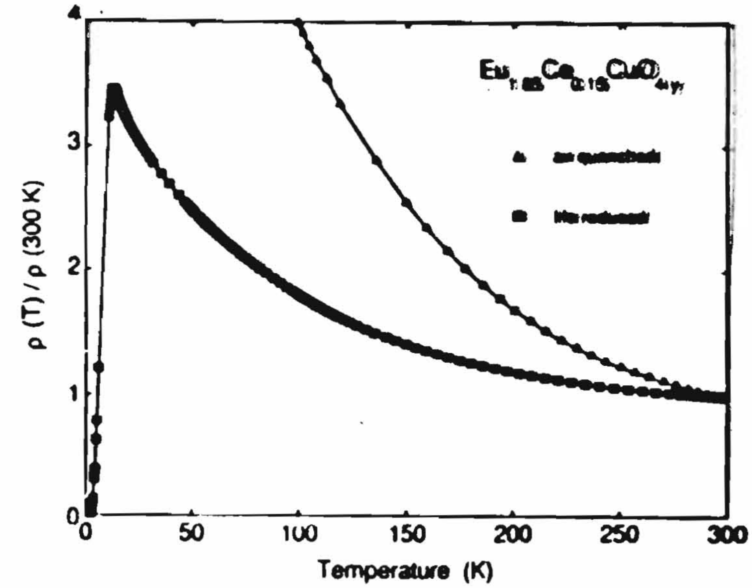


Fig. 3. Normalized electrical resistivity, $\rho(T)/\rho(300\ \mathrm{K})$, plotted as a function of temperature T for two $Eu_{1.85}Ce_{0.15}CuO_{4-y}$ specimens (air-quenched from 1100°C, triangles; helium-annealed at 885°C, squares).

$\frac{\partial \rho}{\partial T} < 0$

⇓

anomalously strong magnetic scattering of electron carriers by paramagnetic Nd^{3+} !!

(UCD)

Data from UCSD

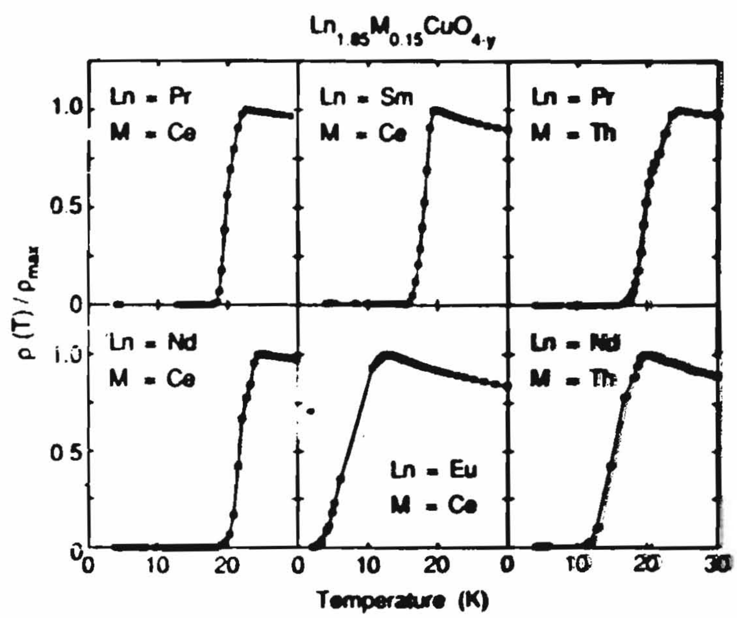


Fig. 4. Normalized electrical resistivity, $\rho(T)/\rho_{max}$, plotted as a function of temperature T over the range $0 \leq T \leq 30$ K for six $Ln_{1.85}M_{0.15}CuO_{4-y}$ electron superconductors. Data for Ln = Pr, Nd, Sm, and Eu, M = Ce, and Ln = Pr and Nd, M = Th are shown. All samples shown were helium-annealed at temperatures in the range 885–910°C. Considerable variation of T_c with host and dopant ions is evident.

tance was obtained only for annealing temperatures near 885°C. This specimen exhibited an onset temperature of 12.5 K, a midpoint $T_c^{0.5} \approx 8$ K, and $\Delta T_c \approx 6$ K.

The electrical resistivity, normalized to its maximum value, is shown as a function of temperature T

Two–Step Synthesis

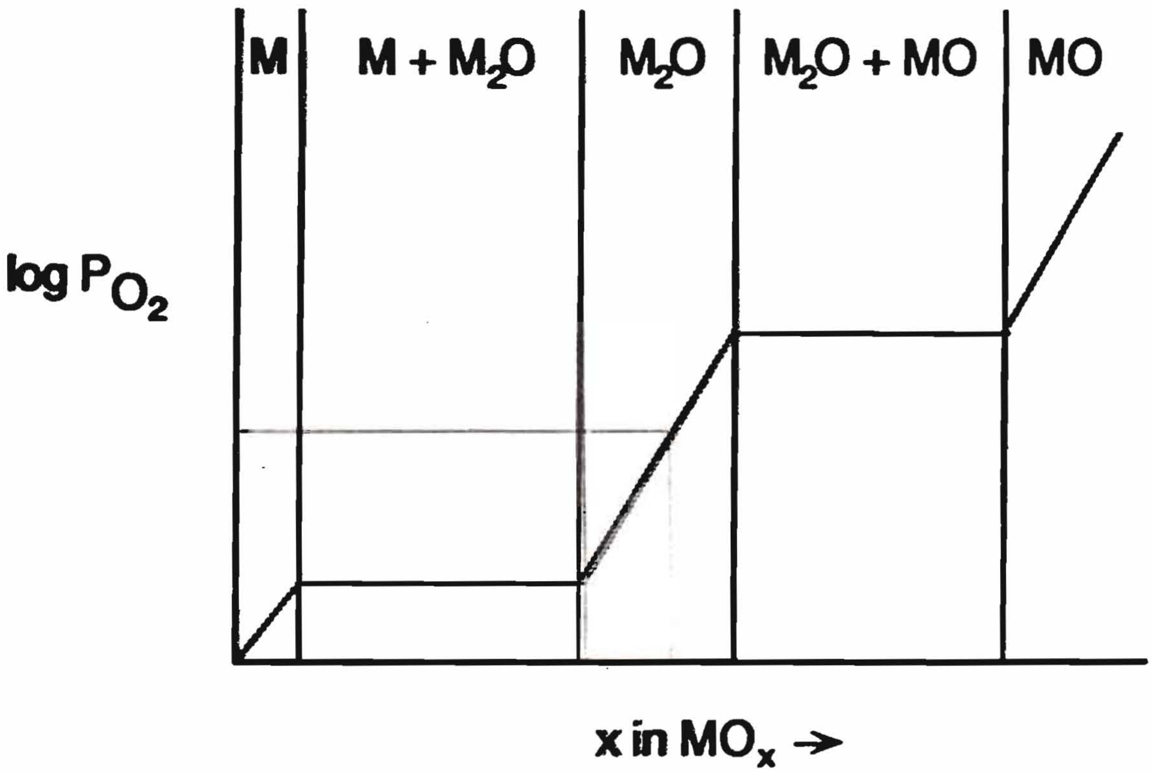
I. $0.5Nd_2O_3 + CeO_2 \rightarrow NdCeO_{3.5}$

- Calcine at 1400 °C, 48 hrs, in air

II. $(1-x)Nd_2O_3 + xNdCeO_{3.5} + CuO \rightarrow$
$Nd_{2-x}Ce_xCuO_4 + 0.25xO_2\uparrow$

- Calcine at 980 °C, 24 hrs, in O_2
- Sinter at 1050 °C, 48 hrs, in O_2
- Anneal at 980 °C, 36 hrs, in Argon
- Quench to 25 °C, 30 sec, in Argon

Phase Stability vs P_{O_2}:



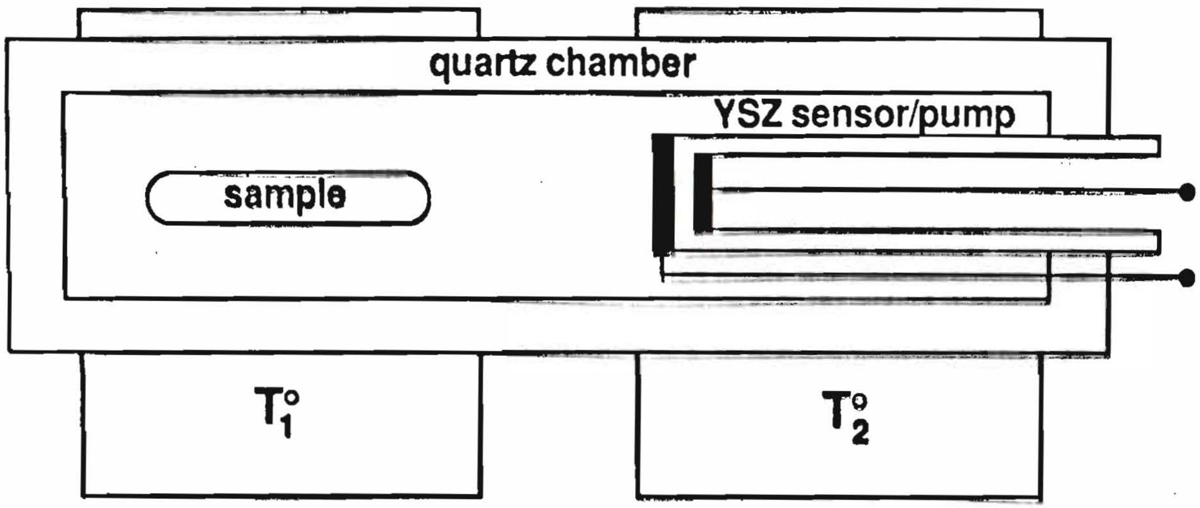
Gibbs Phase Rule:

$F = C + 2 - P$

$= 1$ in single-phase regions for constant T° and P_{Total}

$= 0$ in two-phase regions for constant T° and P_{Total}

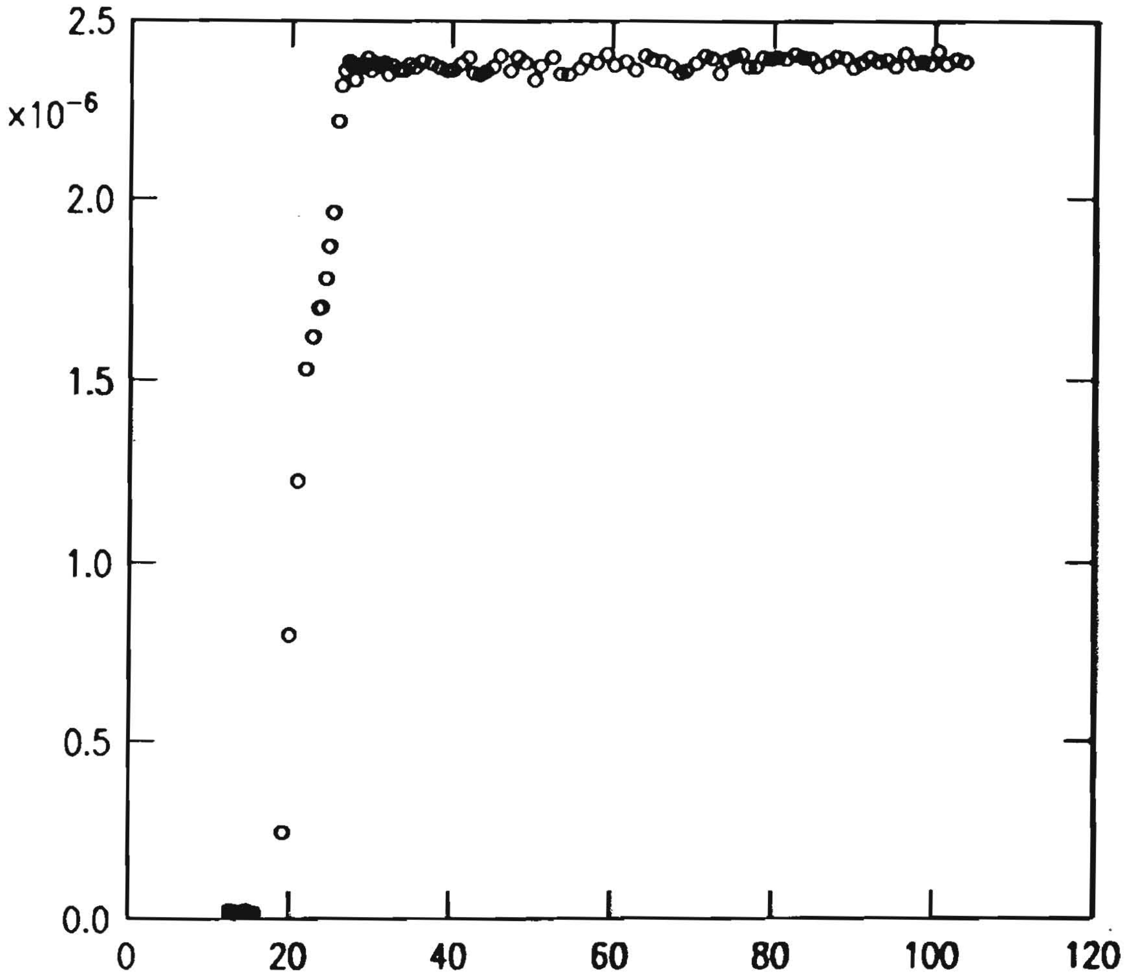
Solid Electrolyte Apparatus:



$$E = -\frac{kT}{4q} \ln \frac{P_{O_2}\text{ (sample)}}{P_{O_2}\text{ (ref. electrode)}}$$

$$\Delta m = (M_O / z_O F) \int I\,dt$$
$$= 8 \times 10^{-10}\text{ g}$$

(for $\int I\,dt = 10^{-5}$ Asec)

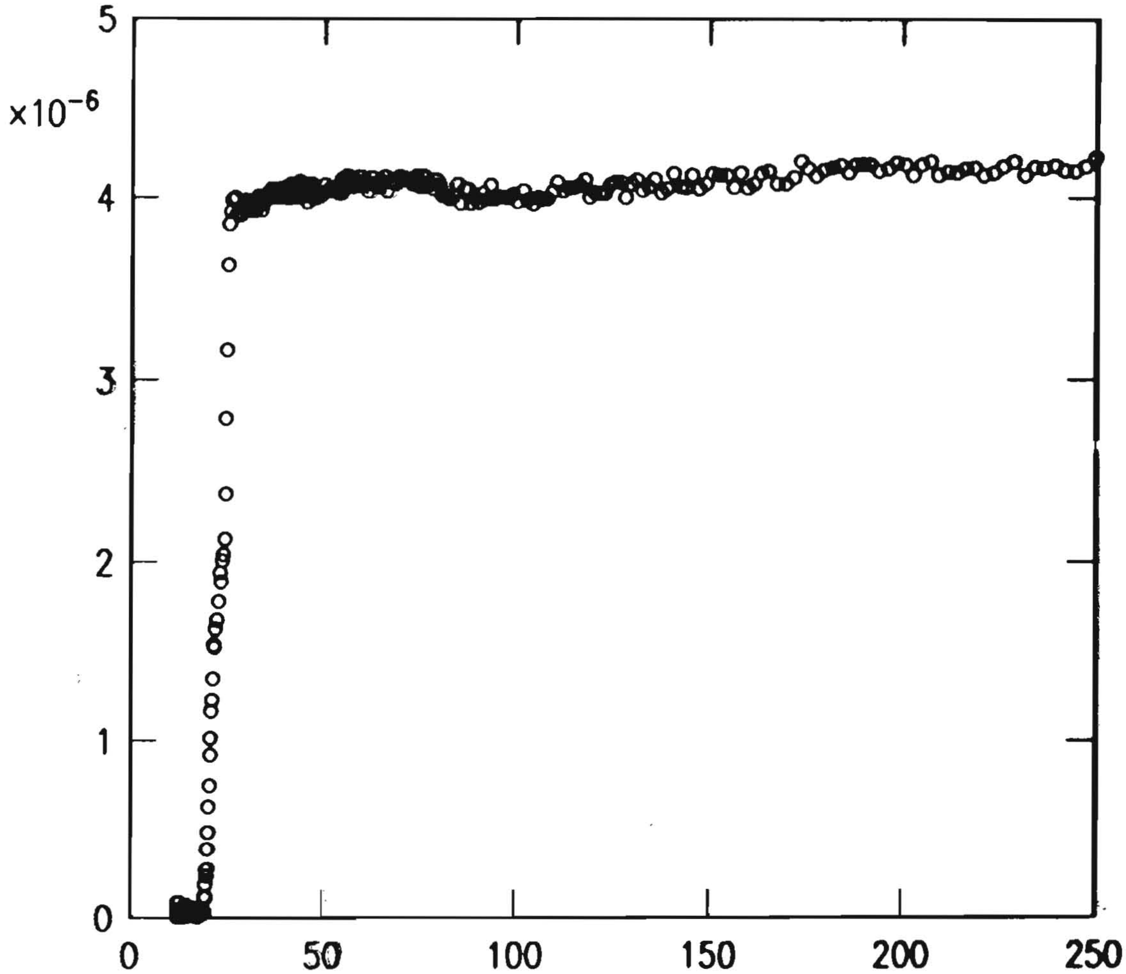


~~Resistivity~~ vs Temperature for Sample: NN682A
Resistance

Quenched

Quenched

$P_{O_2} = 2 \times 10^{-6}$



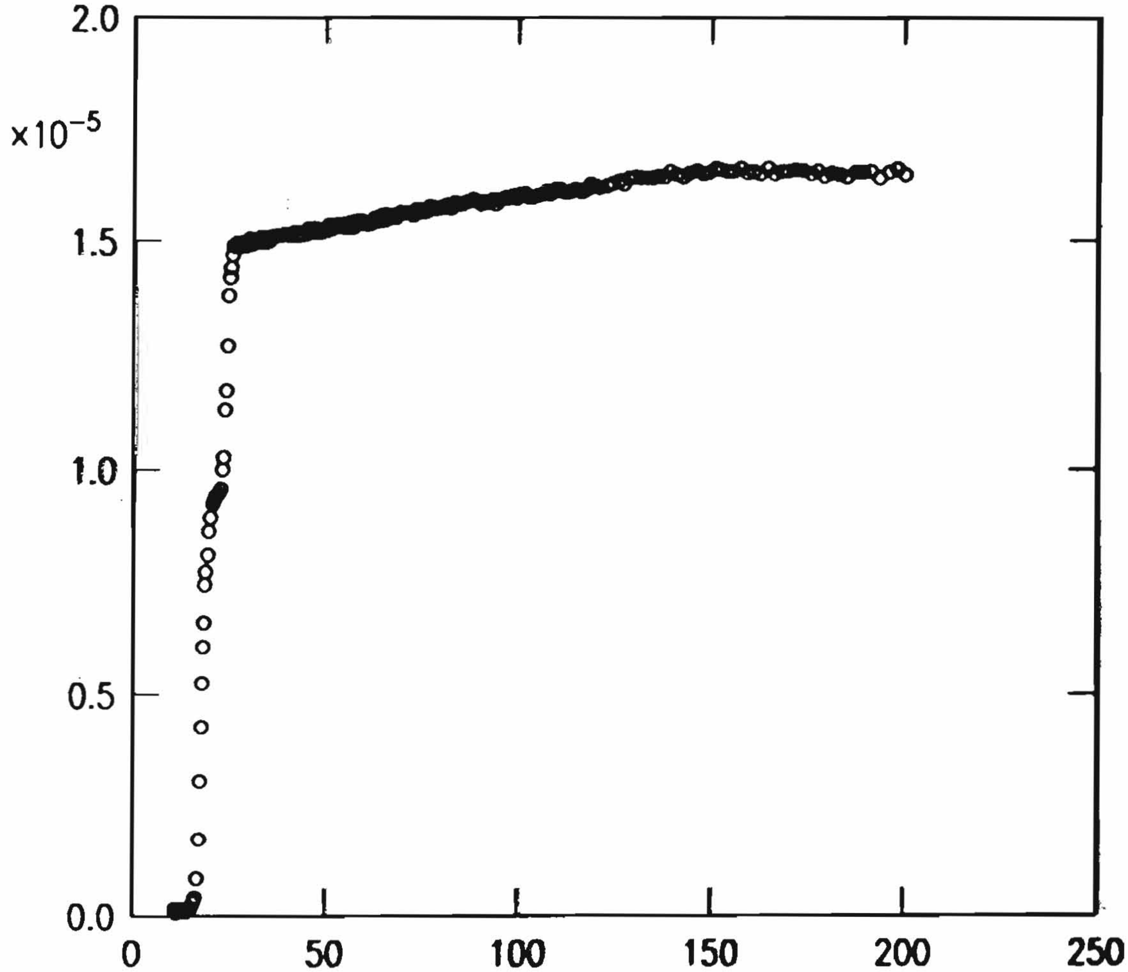
[redacted] vs Temperature for Sample: NN683AA

Resistance

Slow cooled

Quenched

$PO_2 = 1 \times 10^{-6}$

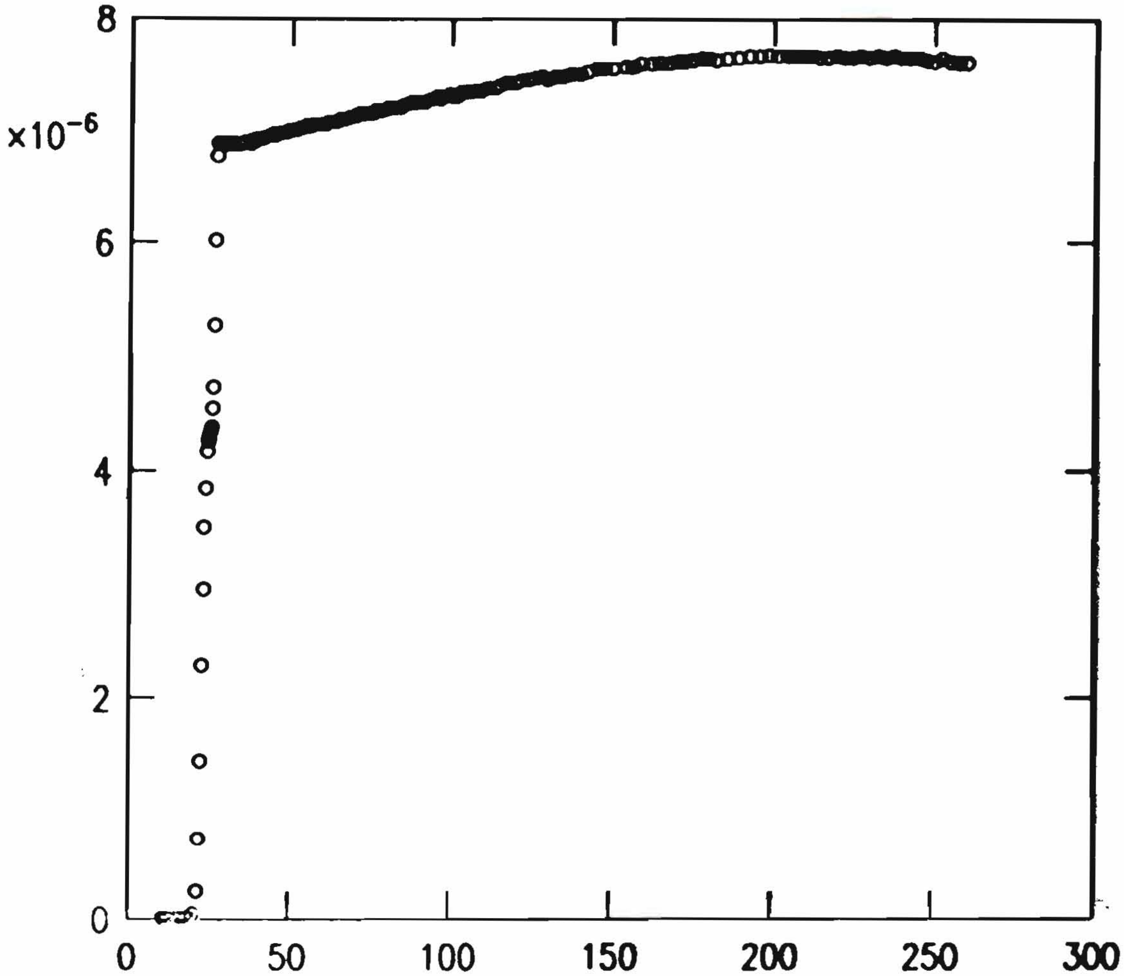


[redacted] vs Temperature for Sample: NN682BB
Resistance

Quenched

Slow cooled

$P_{O_2} = 4 \times 10^{-6}$

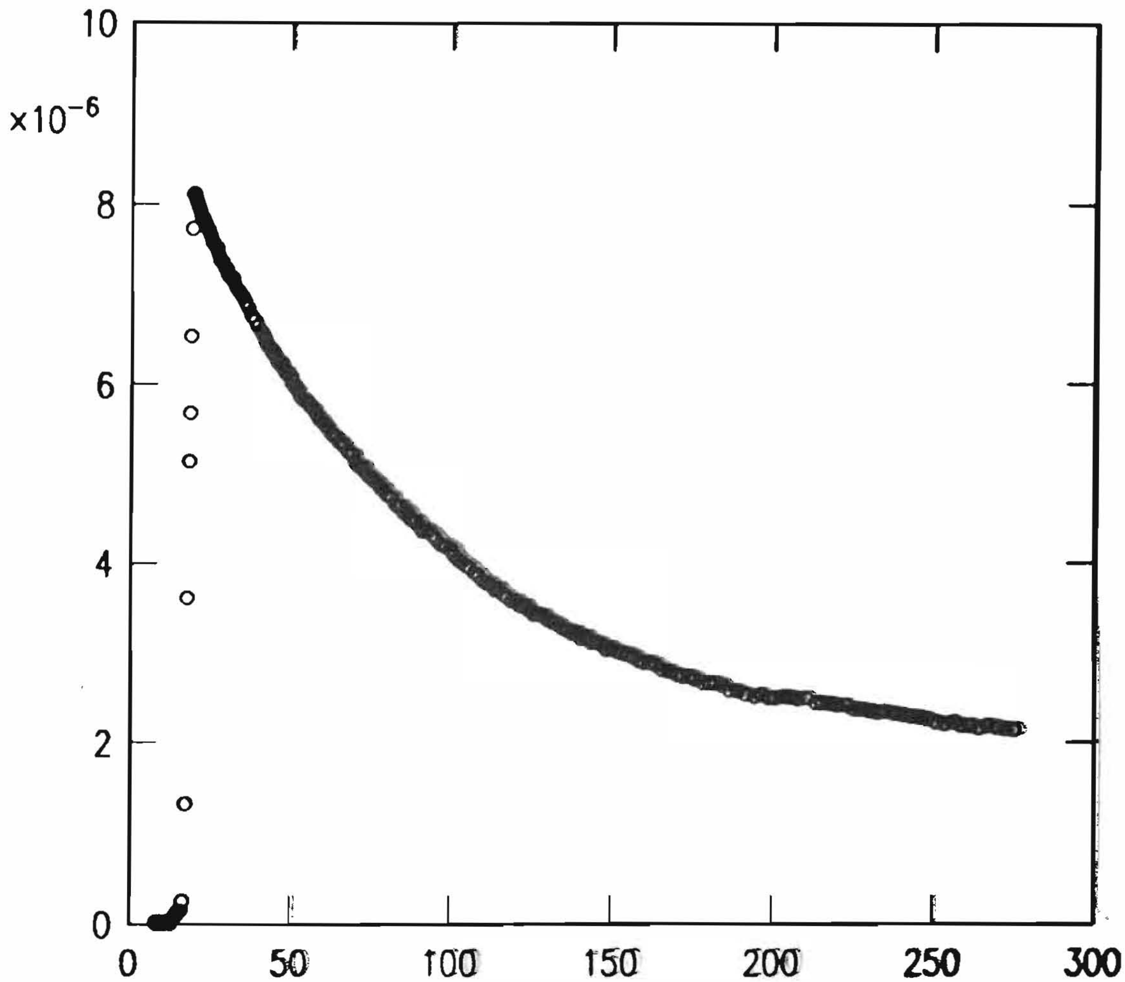


~~Resistivity~~ vs Temperature for Sample: N692
Resistance

slow cooled

slow cooled

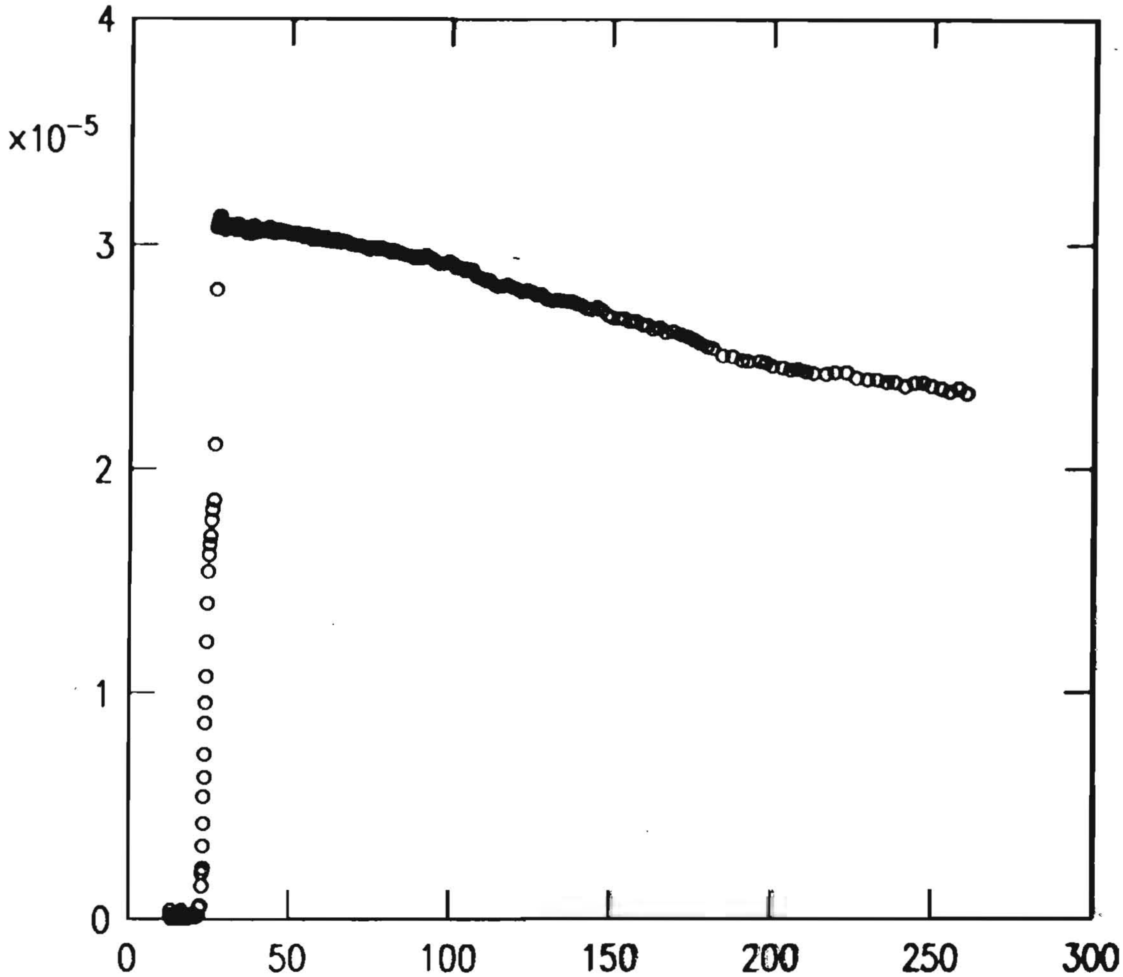
$P_{O_2} = 3.5 \times 10^{-6}$



[redacted] vs Temperature for Sample: NN641
Resistance

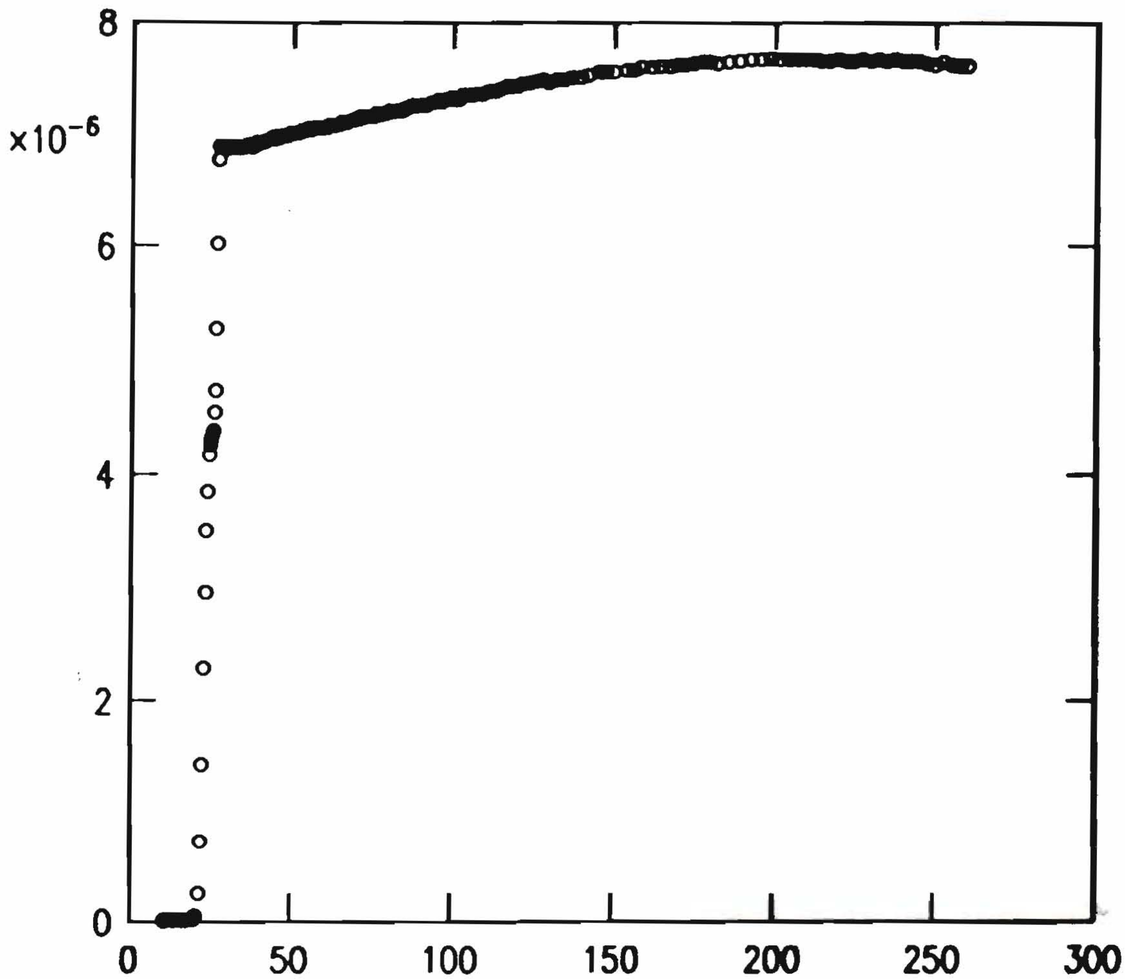
$P_{O_2} = 2.1 \times 10^{-3}$

H.005



~~Resistivity~~ vs Temperature for Sample: NN691
Resistance

$P_{O2} = 6.8 \times 10^{-6}$

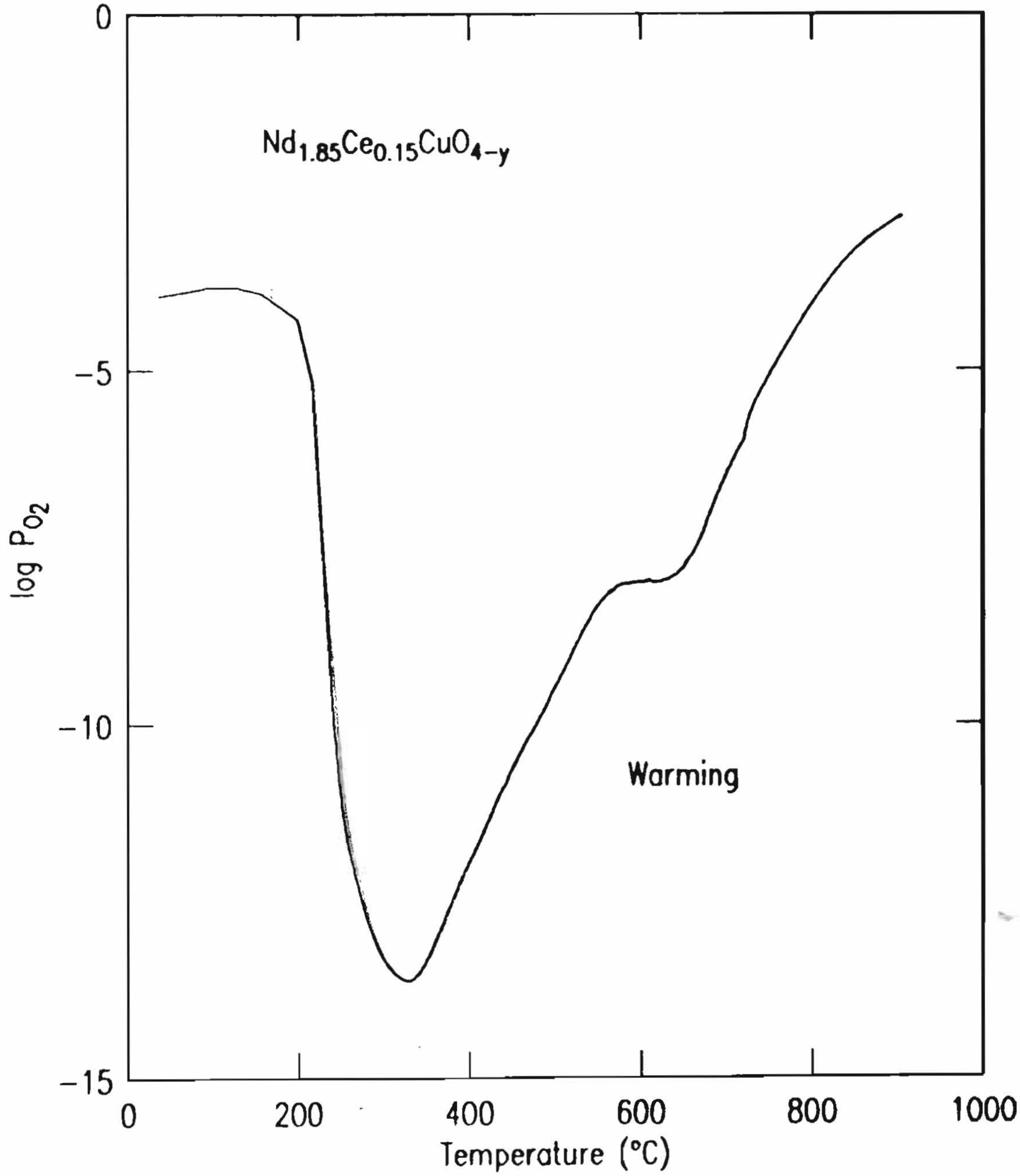


[redacted] vs Temperature for Sample: N692

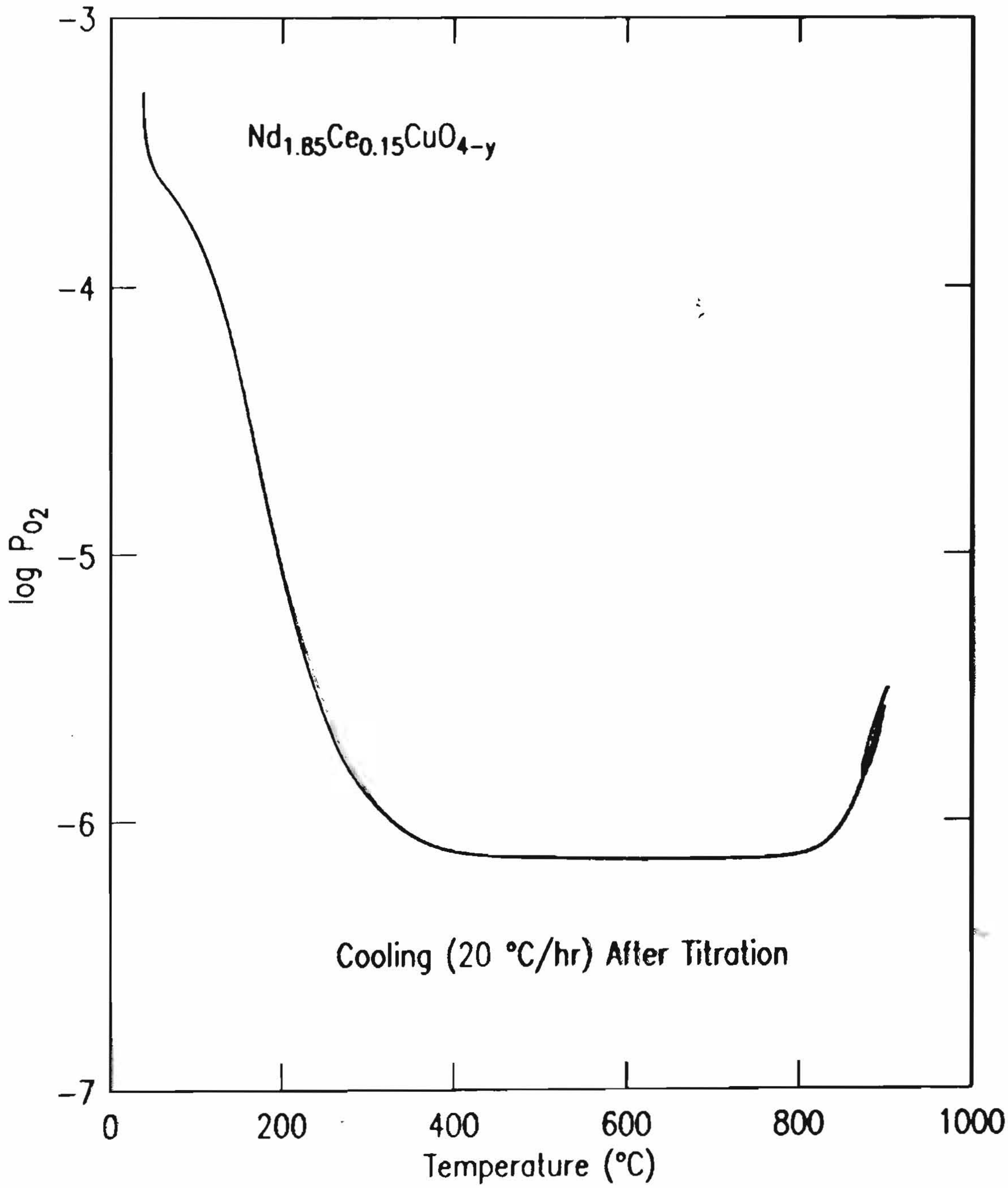
Resistance

O 3.97

$P_{O_2} = 3.05 \times 10^{-6}$

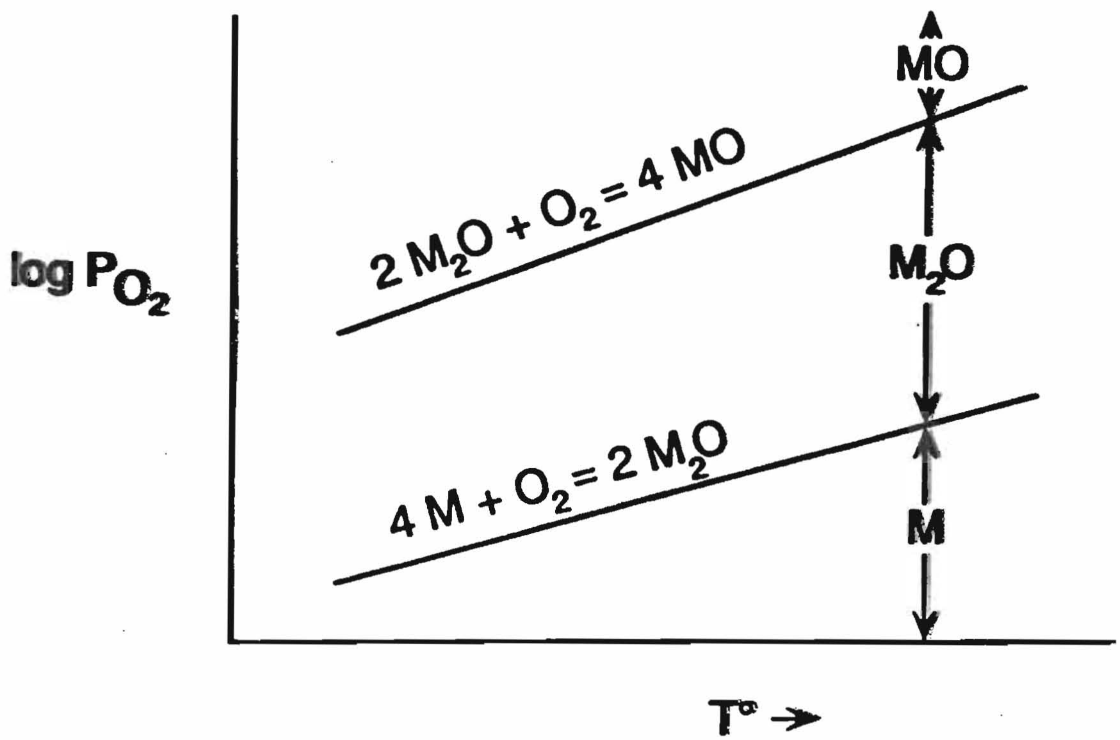


Nd1.85Ce0.15CuO4-y
Warming
log PO2
Temperature (°C)
0
-5
-10
-15
0
200
400
600
800
1000



$Nd_{1.85}Ce_{0.15}CuO_{4-y}$
Cooling (20 °C/hr) After Titration
log P_{O_2}
-3
-4
-5
-6
-7
0
200
400
600
800
1000
Temperature (°C)

Phase Stability vs T°, P_{O_2}:



Conclusions

- Oxygen content of $Nd_{2-x}Ce_xCuO_y$ can be controlled using oxygen coulometric titration.
- The electronic properties of this material depend upon its oxygen content.