Suggested Session:
High-Tc Materials

for the 1992 March Meeting
16-20 March 1992

March Sorting Category:
29a

Electrical and Magnetic Properties of $La_{4-x}Pr_xBaCu_5O_{13-y}$.

M. E. LÓPEZ-MORALES, J. L. HEIRAS and R. ESCUDERO, Materials Institute (IIM), Nat. Auto. U. México (UNAM).

— The compound $La_4BaCu_5O_{13-y}$ is remarkable in that it is one of the very few CuO perovskites that is metallic at all temperatures yet superconducting at none. In addition, it has an unusually high carrier concentration, as estimated from the excess cationic charge in the unit cell, compared to the high-T_C copper oxide compounds. We have investigated the effect of substituting Pr for La in this structure with the objective of studying possible mixed valent effects arising from the Pr cation. We find that it is possible to obtain single phase $La_{4-x}Pr_xBaCu_5O_{13-y}$ for $x \leq 2$, and report the observed electrical and magnetic properties of a sample set within this range.

Prefer Standard Session

Paul M. Grant
IIM - UNAM
CU, Coyoacan 04510
Apdo. Postal 70-360 y 70-284
Mexico, D.F., Mexico

Room 146 at 8:00

subsequent low temperature re-oxidation on the oxygen ordering and Fe distribution in these systems. Monte Carlo simulations using Kawasaki dynamics is used to investigate the Fe cluster formation and its effect on oxygen ordering for various Fe concentrations. The results are in very good agreement with experiments, suggesting that the structure change during the reduction and re-oxidation process can be explained by Fe clustering in CuO plane.

*Work supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No. DE-AC02-76CH00016.

8:24

Q13 3 Investigations of T_c Dependence on Magnetic and Nonmagnetic Ions in $YBa_2[Cu_{1-x}(M_xZn_{1-x})_x]_3O_{7-\delta}$ M.A. CASTRO, S.A. HOFFMAN, G.C. FOLLIS and S.M. DURBIN, *Purdue U.*—In seeming contradiction with BCS theory, previous studies on the response of high-T_c superconductors to the presence of dopants* have not conclusively found a qualitative difference between the effects of magnetic and nonmagnetic impurities on T_c. We are investigating dopant effects on T_c which appear to be sensitive to the magnetic character of the impurity. Apart from magnetic spins, an impurity ion may introduce other perturbations which could mask the effect of spins. The charge carrier concentration, for instance, can be affected if the dopant and host ions have different valences. By simultaneously doping with ions of different valences and magnetic nature, we are able to vary both the charge carrier density and the concentration of magnetic spins. We report on magnetic susceptibility and electrical resistivity measurements on polycrystalline $YBa_2[Cu_{1-x}(M_xZn_{1-x})_x]_3O_{7-\delta}$ (with M=Ga, Fe, Ni) to determine the dependence of T_c on impurity concentration, as well as anomalous dispersive x-ray diffraction measurements on single crystals to determine the dopant site occupancy distribution.

This work is supported by the Indiana Center for Innovative Superconducting Technology and the NSF through Grant DMR 86-57587.

* K. Westerholt *et al.*, Phys. Rev. B 39, 11680 (1989).

8:36

Q13 4

Sn Dopant in $YBa_2Cu_3O_7$ and $YBa_2Cu_4O_8$* S.PRADHAN, Y.WU, J.MOSES and P.BOOLCHAND, University of Cincinnati,---$YBa_2(Cu_{1-x}Sn_x)_4O_8$ samples at x=0.01 and 0.02 have been prepared by sintering the precursors at 220 atm. and 900°C in pure oxygen. Tc of both samples established magnetically reveal a value of 77(1)K. XRD scans of the samples reveal primarily a 1-2-4 phase. ^{119}Sn Mössbauer spectroscopy results reveal in both cases a partially resolved but asymmetric doublet. These results on 1-2-4 will be compare to the results of several studies(1) on 1-2-3, to decode the dopant site location in these layered cuprates.

* Supported by NSF grant DMR-89-02836

(1) T.Saito et al. Physica C171,167(1990) and references there in.

8:48

Q13 5 The Effect of Sr-doping on the Superconducting Transition of Y-Ba-Cu-O System* M.K. Wu, C.C. Chi**, D.H. Chen, S.R. Sheen, M.J. Wang, and J.L. Hsu, Dept. Physics and Materials Science Center, National Tsing-Hua University, Taiwan, ROC; F.Z. Chien, Dept. of Physics, Tamkang University, Taiwan, ROC. — We have achieved the preparation of single phase $Y(Ba_{1-x}Sr_x)_2Cu_3O_7$ compound with x ranging from 0 to 1 by substituting a small amount of Mo for Cu. It was observed that the superconducting transition temperature first decreases linearly with Sr-content until x≃0.4, then a sharp drop in Tc occurs. The T_c for the sample with x=1 is about 40 K. The X-ray structure analysis shows that the crystal symmetry changes from orthorhombic to tetragonal at the critical concentration, where T_c exhibits a sharp drop. Detail results on the Hall coefficient, normal state resistivity, and Raman spectrum measurements will be presented and discussed.

* Supported in part by ROC NSC Grant NSC80-0208-M007-95.

** Permanent address: IBM, T.J. Watson Research Center, Yorktown heights, NY 10598

9:00

Q13 6

The Effect of Sr-substitution on the Y-site of the $YBa_2Cu_3O_7$ Superconducting Structure. B.H. MA, C.U. SEGRE, Illinois Institute of Technology, M.K. ANIS, A.A. GILL, S.A. HAYAT, Z. IQBAL, K.E. LIPINSKA-KALITA, F.C. MATACOTTA, M.M. SAIH, P. STASTNY, International Centre for Theoretical Physics — The solubility range of Sr on the Y-site in the $YBa_2Cu_3O_7$ Structure was studied using two series of compounds: $(Gd_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-\delta}$ and $(Sm_{1-x}Sr_x)(Ba_{1.5}Sr_{0.5})Cu_3O_{7-\delta}$. Structural, compositional and transport data are reported as functions of Sr-content, x and sample preparation temperature. The Sm samples show systematic increases in T_{C0} with both Sr-content and annealing temperature. The difference in behavior between Gd and Sm-based samples is most likely related to their differing ionic sizes. Increasing the Sr content seems to prevent the trivalent Sm from occupying the Ba site and thus reducing T_C. Measurements of screening fraction made by a.c. susceptibility at 4K show that with one exception, a decrease with increasing x (Sr content) but an increase with increasing annealing temperature. The Sm-based samples annealed at 970°C, however, show a relatively constant screening factor as a function of composition.

9:12

Q13 7 Electrical and Magnetic Properties of $La_{4-x}Pr_xBaCu_5O_{13-y}$. M. E. LÓPEZ-MORALES, J. L. HEIRAS and R. ESCUDERO, Materials Institute (IIM), Nat. Auto. U. México (UNAM). — The compound $La_4BaCu_5O_{13-y}$ is remarkable in that it is one of the very few CuO perovskites that is metallic at all temperatures yet superconducting at none. In addition, it has an unusually high carrier concentration, as estimated from the excess cationic charge in the unit cell, compared to the high-T_C copper oxide compounds. We have investigated the effect of substituting Pr for La in this structure with the objective of studying possible mixed valent effects arising from the Pr cation. We find that it is possible to obtain single phase $La_{4-x}Pr_xBaCu_5O_{13-y}$ for $x \leq 2$, and report the observed electrical and magnetic properties of a sample set within this range.

9:24

Q13 8 Effects of Oxygen Order on Superconductivity in Substituted $RBa_2Cu_3O_{7-\delta}$ Superconductors.* P. KOSTIĆ, B. W. VEAL, A. P. PAULIKAS, and J. W. DOWNEY, Materials Science Division, Argonne National Laboratory.--- We have extensively studied the effect of oxygen vacancy order in reduced $YBa_2Cu_3O_{7-\delta}$ (Y123): vacancies tend to order forming chains in the b-direction and the superconducting T_c rises, apparently a consequence of increased hole concentration. Annealing disordered samples at room temperature can result in a rise of nearly 30 K in T_c. When cations are substituted however, it appears that alternate forms of oxygen ordering can occur. When reduced samples of Y123 or Gd123, with Sr replacing one-half of the Ba atoms, are quenched from temperatures in the range $75 > T_q > 190°C$, T_c declines when the samples are permitted to anneal at room temperature. These results suggest that an ordering process occurs in the substituted samples at low temperatures that reduces the carrier concentration. In contrast to Y123, this might be accomplished by a reduction in the concentration of 2-coordinated (monovalent) Cu atoms as a result of the ordering.

*Work supported by the U.S. Department of Energy, BES-Materials Sciences, under contract #W-31-109-ENG-38.

Electrical and Magnetic Properties of $La_{4-x}Pr_xBaCu_5O_{13\pm\delta}$

M. E. Lopez-Morales
F. Morales
J. L. Heiras
R. Escudero
P. M. Grant

IIM – UNAM

To be reported at
1992 APS March Meeting
Indianapolis, Indiana

GRANT

Mat. Res. Bull., Vol. 20, pp. 667-671, 1985. Printed in the USA.
0025-5408/85 $3.00 + .00

$La_4 Ba Cu_5 O_{13.4}$

THE OXYGEN DEFECT PEROVSKITE $BaLa_4Cu_5O_{13.4}$, A METALLIC CONDUCTOR

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(Received March 14, 1985; Refereed)

ABSTRACT

A new oxygen defect perovskite $BaLa_4Cu_5O_{13.4}$, characterized by a mixed valence of copper has been isolated ; the parameters of the tetragonal cell are closely related to that of the cubic perovskite: $a = 8.644(4)$ Å $= a_p\sqrt{5}$ and $c = 3.867(3)$ Å $= a_p$. The X-ray diffraction study shows that the atoms are displaced from their ideal positions in the cubic cell, owing to the presence of ordered oxygen vacancies. The study of conductivity, magnetic susceptibility and thermoelectric power versus temperature shows that this oxide is a very good metallic conductor.

INTRODUCTION

Oxygen defect perovskites, have been more extensively studied these last years owing to their potential applications in catalysis, electrocatalysis or as gauges (1-3). In this respect mixed valence copper oxides offer a wide field for investigation : several perovskites (4) or perovskite-related structures have been isolated (5-6). These materials in which copper takes several coordinations simultaneously and a valence state intermediate between II and III can intercalate large amounts of oxygen according to the oxygen pressure and the temperature. Their electron transport properties ranging from semi-conductive to metallic (7) are closely correlated to the amount of intercalated oxygen.

The present paper deals with a new oxygen defect perovskite $BaLa_4Cu_5O_{13.4}$, which is like $La_3Ba_3Cu_6O_{14+\delta}$ (4) a mixed valence copper oxide but whose behavior is quite different.

EXPERIMENTAL

Synthesis

Samples were prepared in platinum crucible and in air from appropriate mixtures of dried oxides La_2O_3, CuO and carbonate $BaCO_3$. The mixtures were first heated a few hours at 900°C, ground and heated at 1000°C during several hours. They were then ground again, and mixed with an organic binder, compressed into bars and then slowly heated up to 1000°C. After 24 hours or more at 1000°C, the bars were finally quenched to room temperature. The use of a binder was necessary to avoid that the compressed bars break before

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Possible High T_c Superconductivity in the Ba – La – Cu – O System

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IBM Zürich Research Laboratory, Rüschlikon, Switzerland

Received April 17, 1986

Metallic, oxygen-deficient compounds in the Ba – La – Cu – O system, with the composition $Ba_xLa_{5-x}Cu_5O_{5(3-y)}$ have been prepared in polycrystalline form. Samples with $x = 1$ and 0.75, $y > 0$, annealed below 900 °C under reducing conditions, consist of three phases, one of them a perovskite-like mixed-valent copper compound. Upon cooling, the samples show a linear decrease in resistivity, then an approximately logarithmic increase, interpreted as a beginning of localization. Finally an abrupt decrease by up to three orders of magnitude occurs, reminiscent of the onset of percolative superconductivity. The highest onset temperature is observed in the 30 K range. It is markedly reduced by high current densities. Thus, it results partially from the percolative nature, bute possibly also from $2D$ superconducting fluctuations of double perovskite layers of one of the phases present.

I. Introduction

"At the extreme forefront of research in superconductivity is the empirical search for new materials" [1]. Transition-metal alloy compounds of A 15 (Nb_3Sn) and B 1 (NbN) structure have so far shown the highest superconducting transition temperatures. Among many A 15 compounds, careful optimization of Nb – Ge thin films near the stoichiometric composition of Nb_3Ge by Gavalev et al. and Testardi et al. a decade ago allowed them to reach the highest $T_c =$ 23.3 K reported until now [2, 3]. The heavy Fermion systems with low Fermi energy, newly discovered, are not expected to reach very high T_c's [4].

Only a small number of oxides is known to exhibit superconductivity. High-temperature superconductivity in the Li – Ti – O system with onsets as high as 13.7 K was reported by Johnston et al. [5]. Their x-ray analysis revealed the presence of three different crystallographic phases, one of them, with a spinel structure, showing the high T_c [5]. Other oxides like perovskites exhibit superconductivity despite their small carrier concentrations, n. In Nb-doped $SrTiO_3$, with $n = 2 \times 10^{20}$ cm^{-3}, the plasma edge is below the highest optical phonon, which is therefore unshielded [6]. This large electron-phonon coupling allows a T_c of 0.7 K [7] with Cooper pairing. The occurrence of high electron-phonon coupling in another metallic oxide, also a perovskite, became evident with the discovery of superconductivity in the mixed-valent compound $BaPb_{1-x}Bi_xO_3$ by Sleight et al., also a decade ago [8]. The highest T_c in homogeneous oxygen-deficient mixed crystals is 13 K with a comparatively low concentration of carries $n = 2$–4×10^{21} cm^{-3} [9]. Flat electronic bands and a strong breathing mode with a phonon feature near 100 cm^{-1}, whose intensity is proportional to T_c, exist [10]. This last example indicates that within the BCS mechanism, one may find still higher T_c's in perovskite-type or related metallic oxides, if the electron-phonon interactions and the carrier densities at the Fermi level can be enhanced further.

Strong electron-phonon interactions in oxides can occur owing to polaron formation as well as in mixed-valent systems. A superconductivity (metallic) to bipolaronic (insulator) transition phase diagram was proposed theoretically by Chakraverty [11]. A mechanism for polaron formation is the Jahn-Teller effect, as studied by Höck et al. [12]. Isolated Fe^{4+}, Ni^{3+} and Cu^{2+} in octahedral oxygen environment

"CRYSTAL" RADII OF Ln^{3+} IONS

Table IV. Comparison of the Cu(2) - Cu(2) interplanar, or "slot", distance d_{Slot}, with source referenced, with increasing trivalent state ionic radii R_{Ln} for various rare earth elements Ln in $LnBa_2Cu_3O_7$. Values of ionic radii are from Ref. 30. Data from this Table used in constructing Fig. 4. Distance units are in Å.

Ln	d_{Slot}	Ref.	R_{Ln}
Er	3.350	a	1.144
Ho	3.367	b	1.155
Y	3.369	c	1.159
Gd	3.395	d	1.193
Nd	3.513	a	1.249
Pr	3.554	This Work	1.266
La	3.676	e	1.30

[a] S. J. La Placa, unpublished data.

[b] Reference 6.

[c] Reference 26.

[d] J. A. Campá, J. M. Gómez de Salazar, E. Gutiérrez-Puebla, M. A. Monge, I. Rasines and C. Ruiz-Valero, Phys. Rev. B37, 529 (1988).

[e] M. Izumi, K. Uchinokura, A. Maeda and S. Tanaka, Jpn. J. Appl. Phys. 26, L1555 (1987).

$La_{4-x}Pr_xBaCu_5O_{13\pm\delta}$
Synthetic Procedure

- Mix stoichiometric amounts of La_3O_2, $BaCO_3$ and CuO
- Grind in light organic liquid (acetone)
- Eliminate CO_2 by baking at 900 C

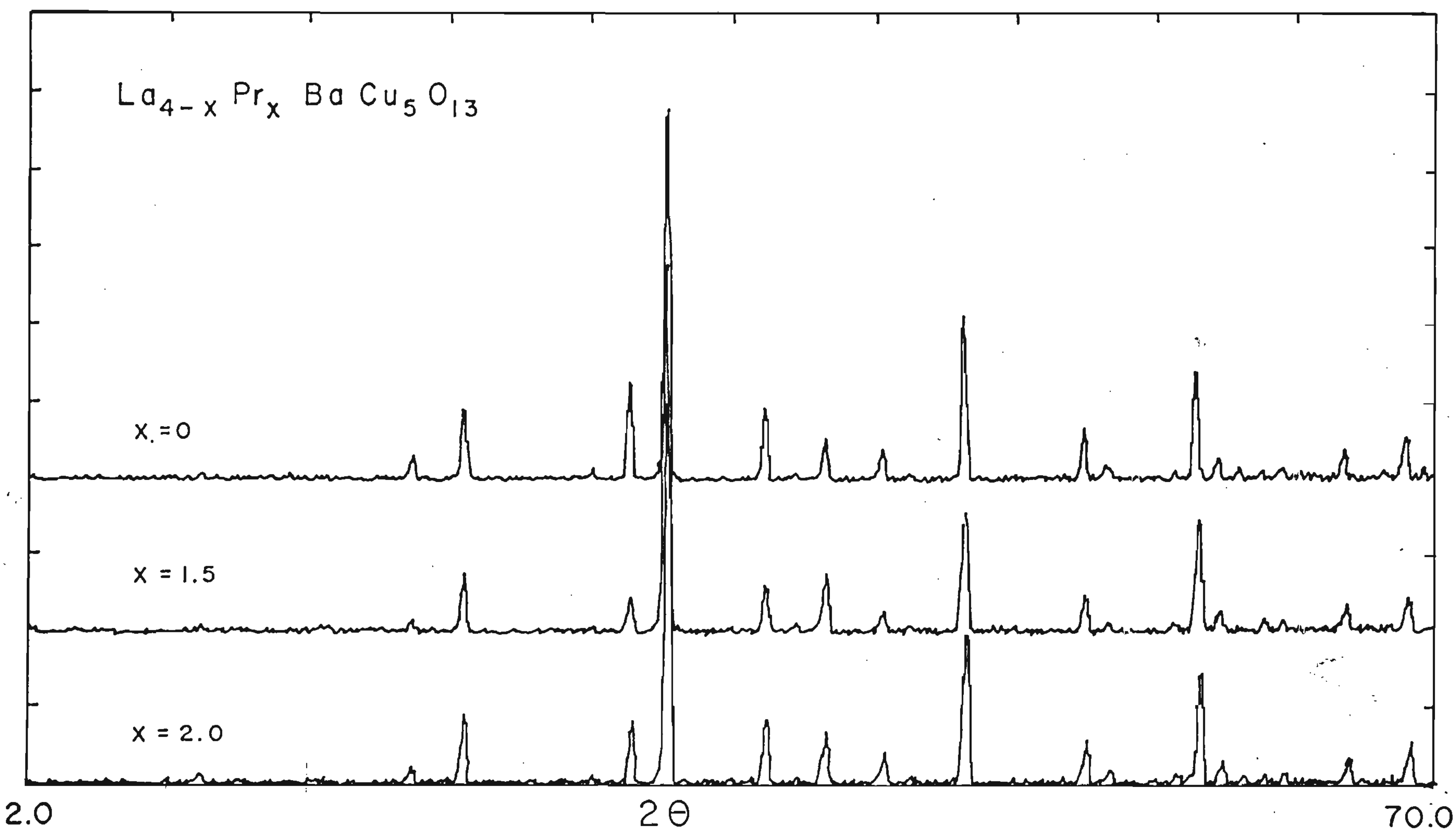
- Grind in acetone again
- Calcine at 950 C
- Mix and grind product with an low MW organic binder (ZYP "HTSC Vehicle")
- Calcine at 950 C
- Dry-grind product
- Final calcine at 970 C

- Dry-grind product
- Press into pellets at 6 metric tons
- Sinter in air at 990 C

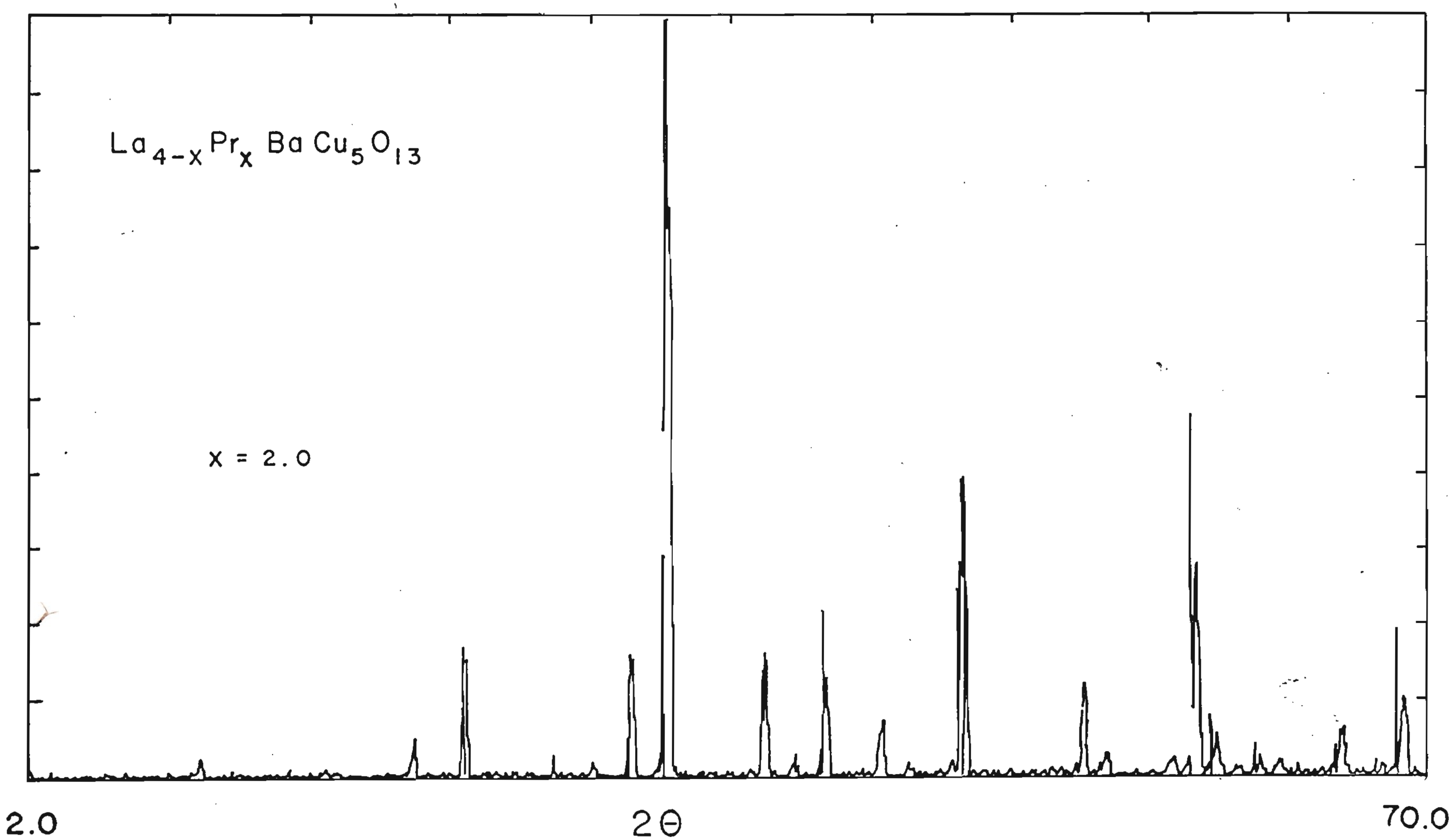
$La_{4-x}Pr_xBaCu_5O_{13\pm\delta}$ Synthetic Procedure

Caveats

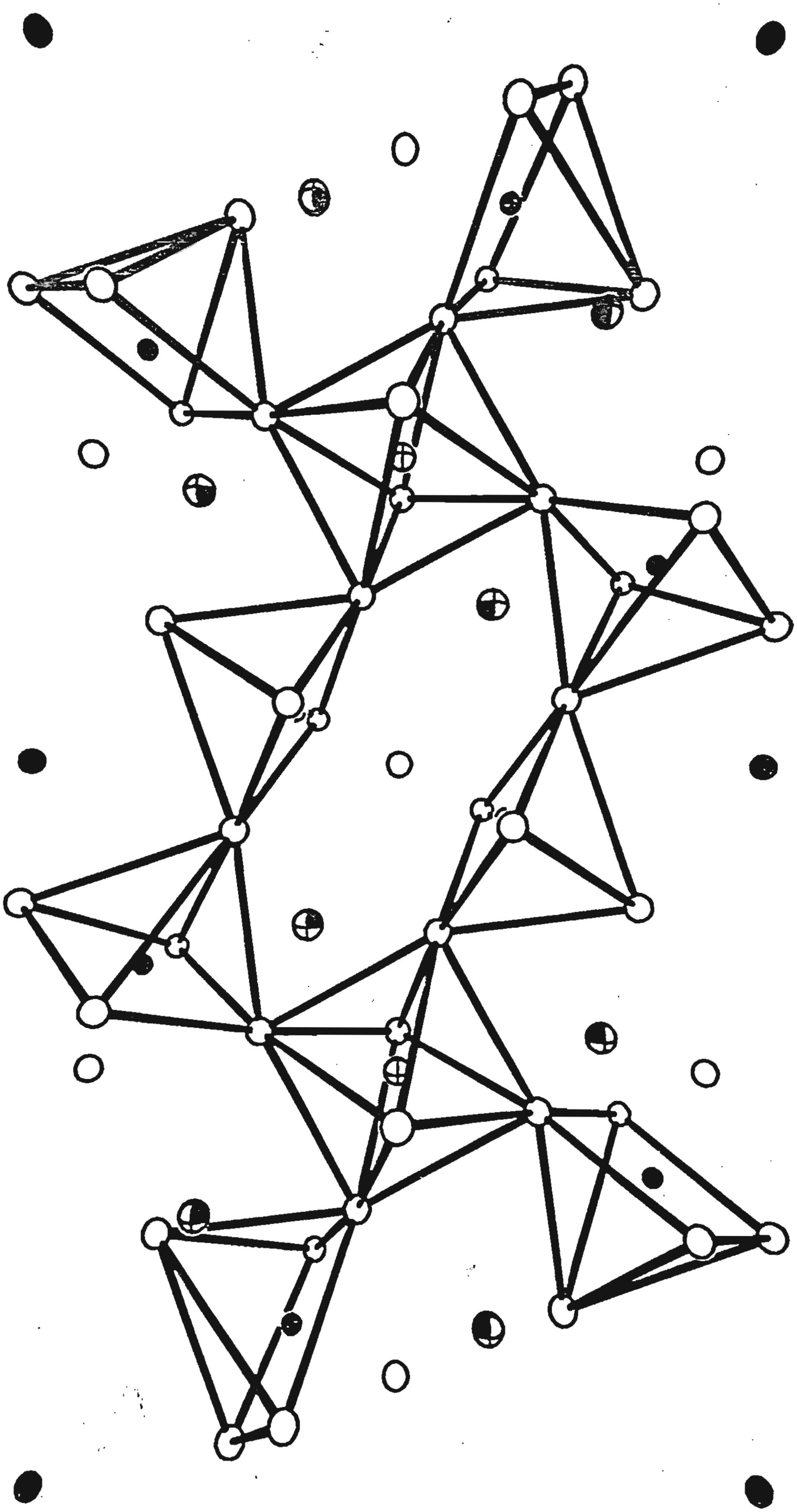
- Must dry La_3O_2 at 950 C prior to weighing
- First calcine at temperature not greater than 900 C in order to prevent melting
- Organic binder helps homogenize final calcine mixture
- Dry grinding needed to eliminate residual traces of binder
- NB: Long calcine periods (~ days) needed as Pr concentration increases due to low diffusion rate of this cation

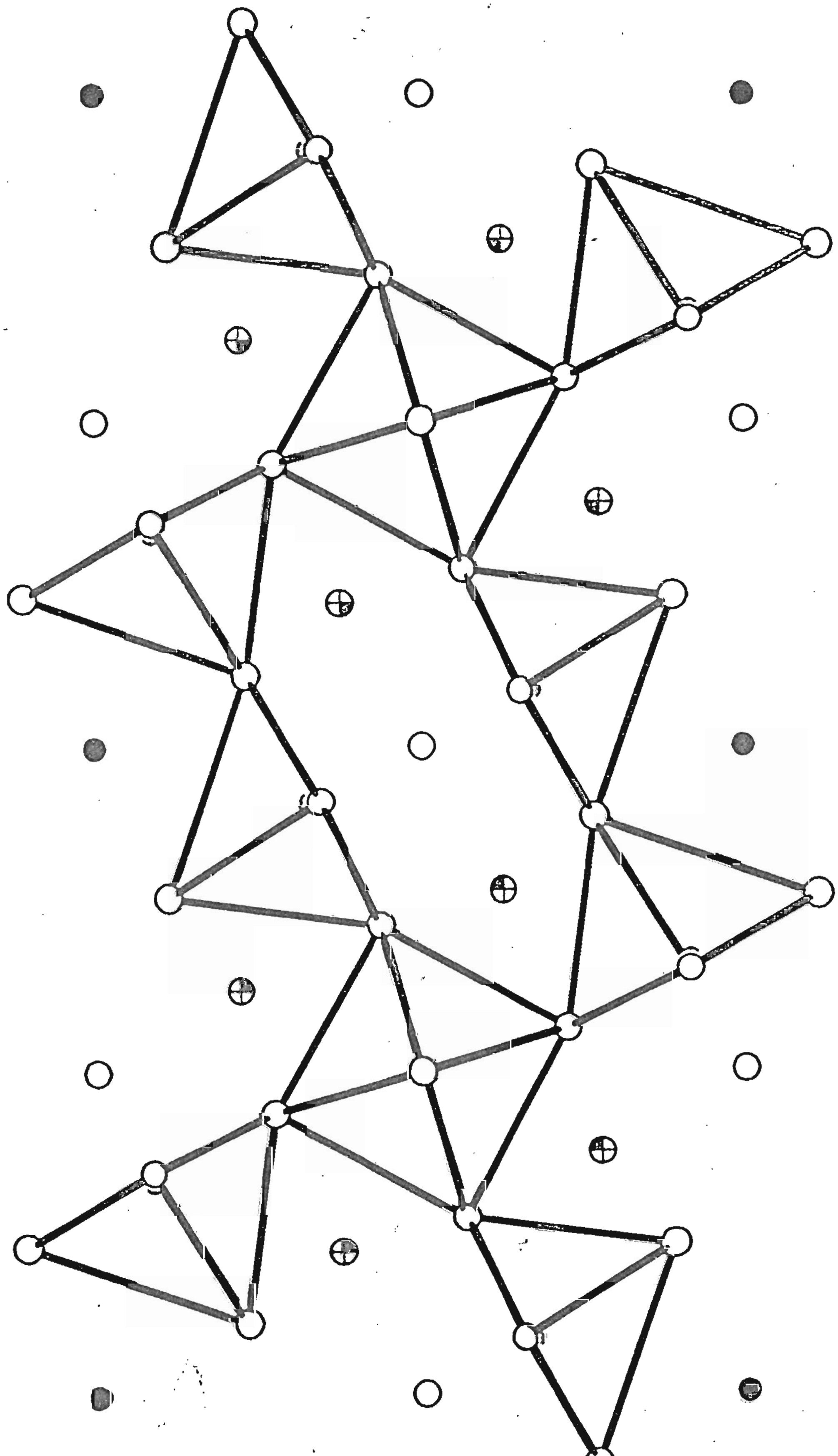


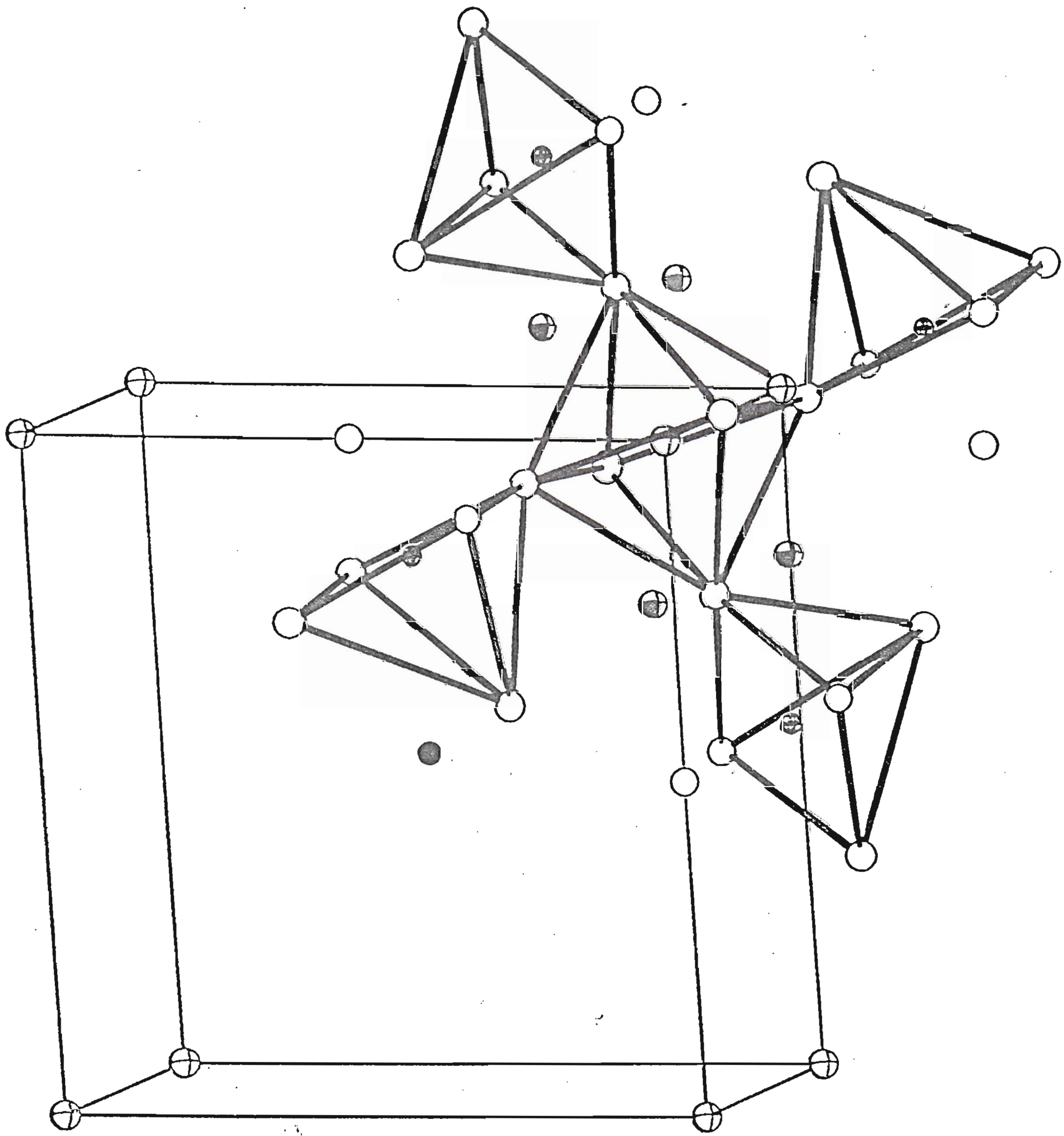
La4-x Prx Ba Cu5 O13
x = 0
x = 1.5
x = 2.0
2.0
2Θ
70.0

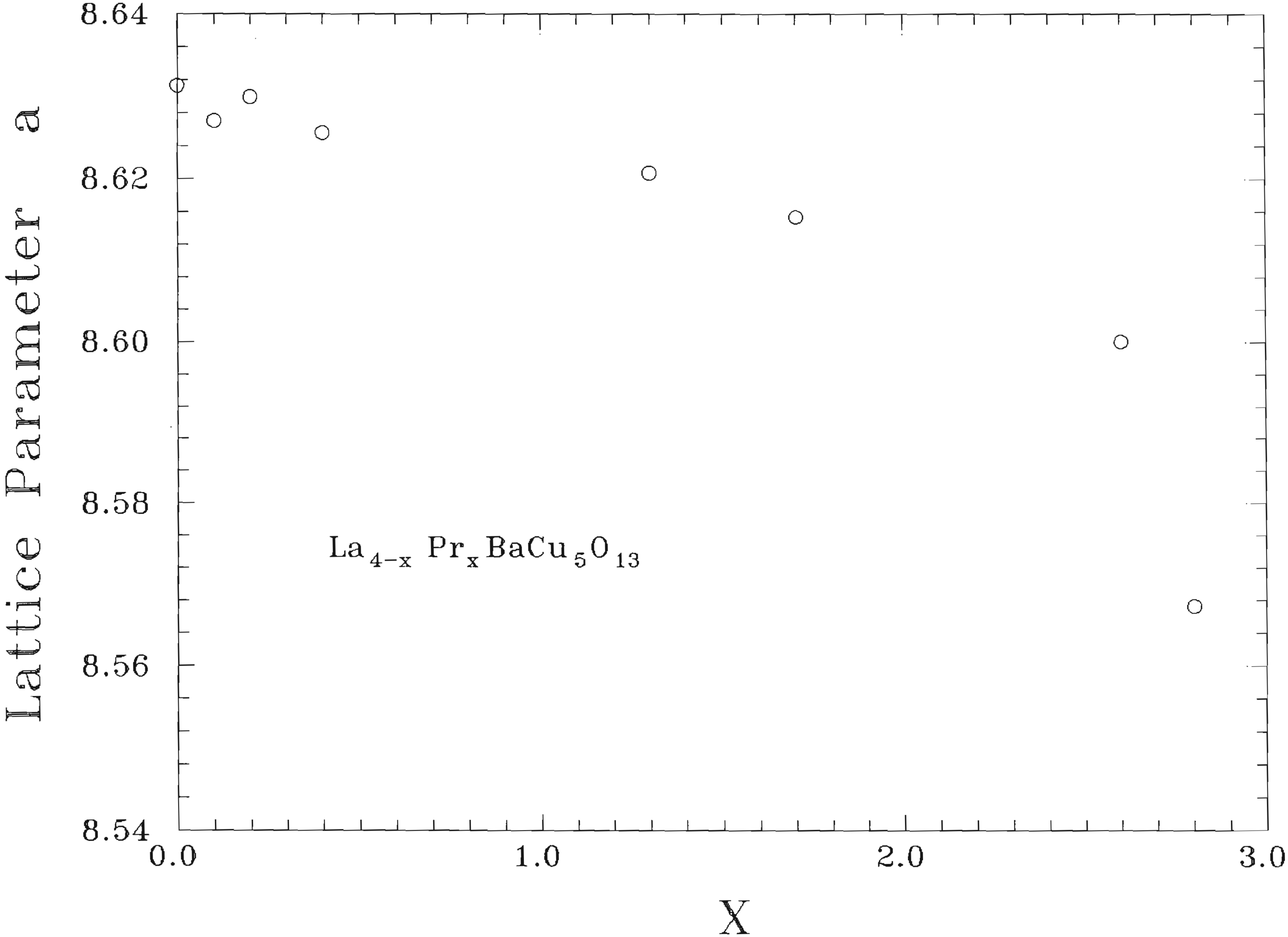


$La_{4-x}Pr_x BaCu_5O_{13}$
x = 2.0
2.0
2Θ
70.0







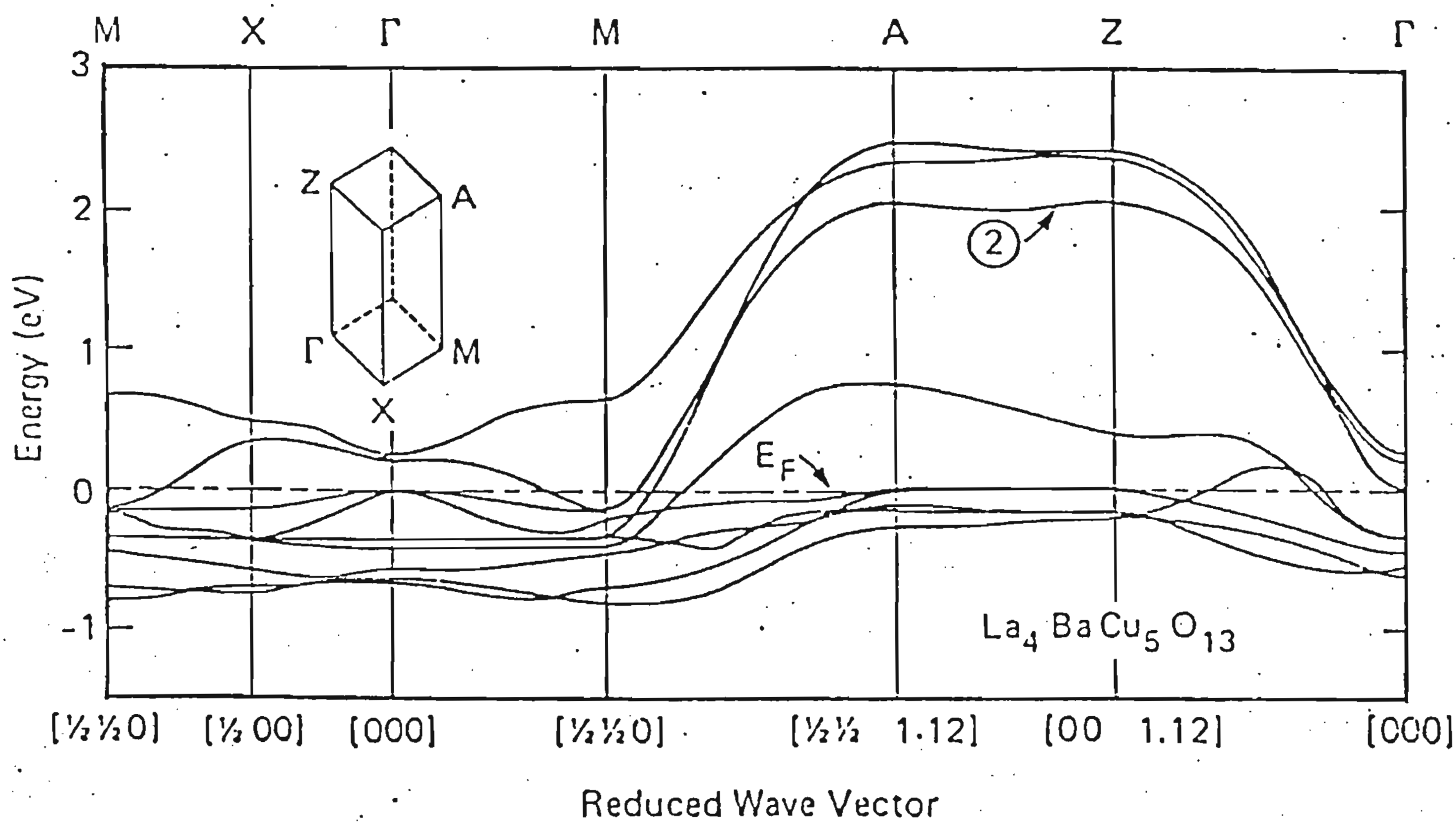


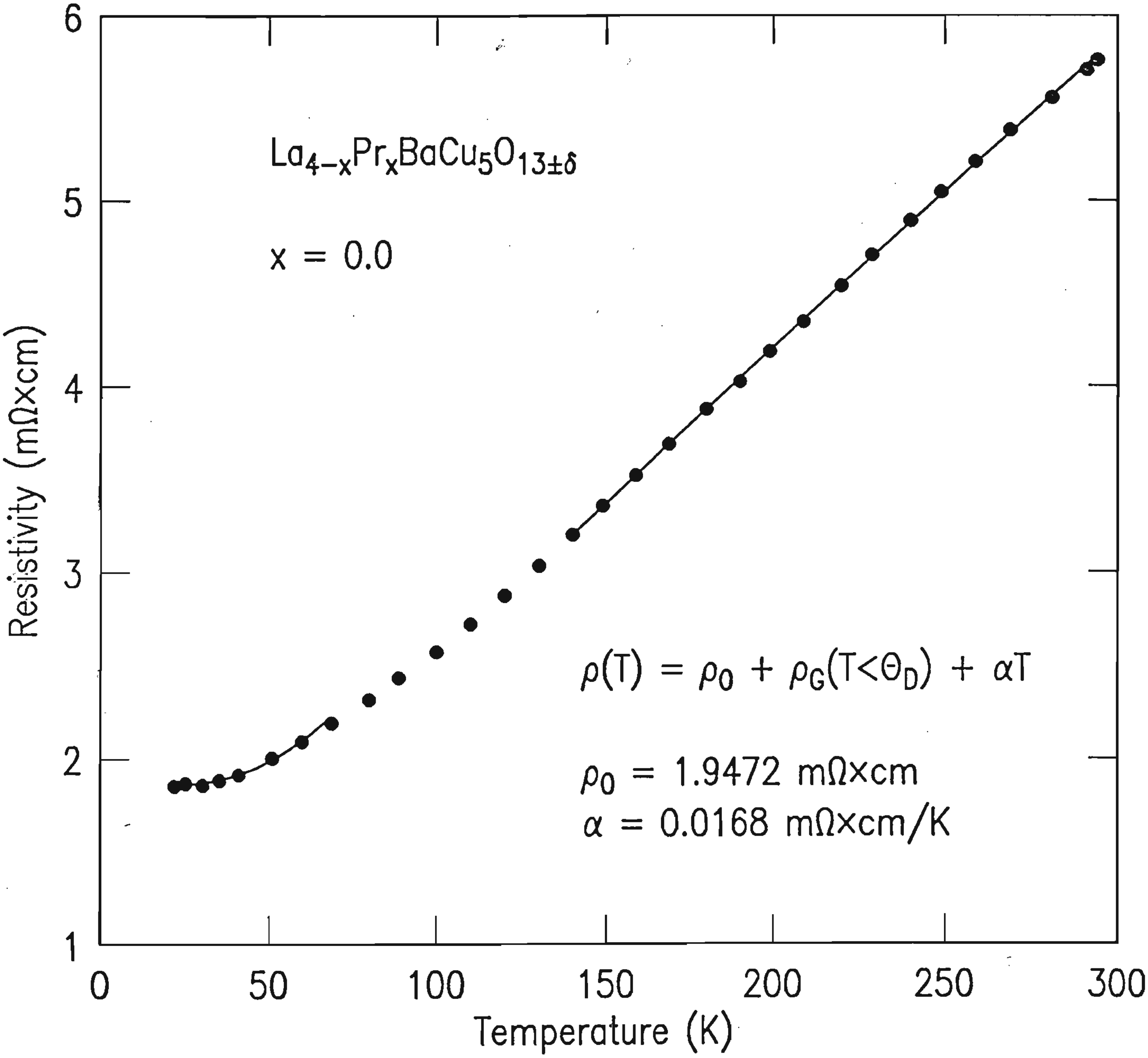
8.64
8.62
8.60
8.58
8.56
8.54
Lattice Parameter a
0.0
1.0
2.0
3.0
X
La 4-x Pr x BaCu 5 O 13

Band Structure of $La_{4-x}Pr_xBaCu_5O_{13\pm\delta}$

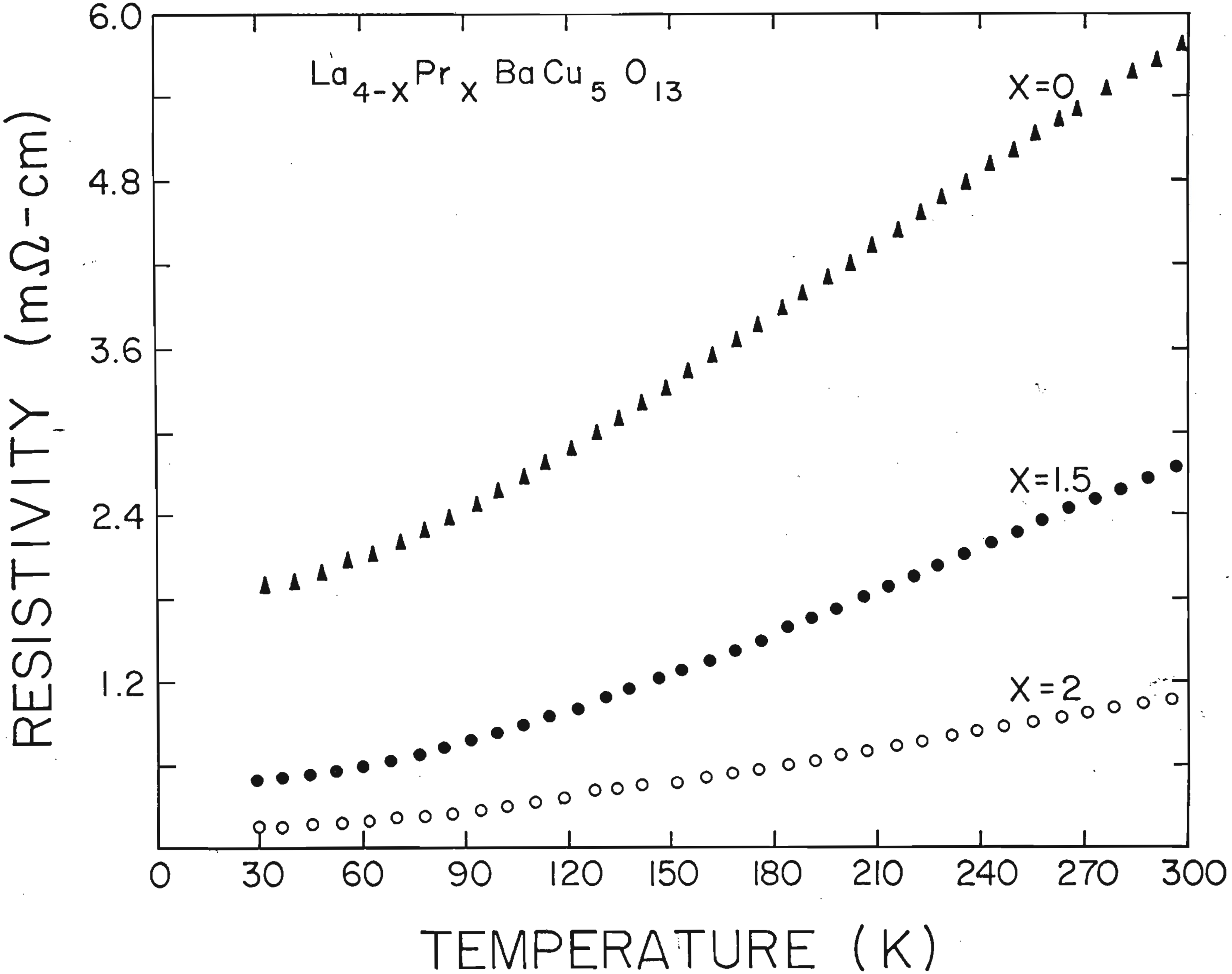
Herman, Kasowski and Hsu

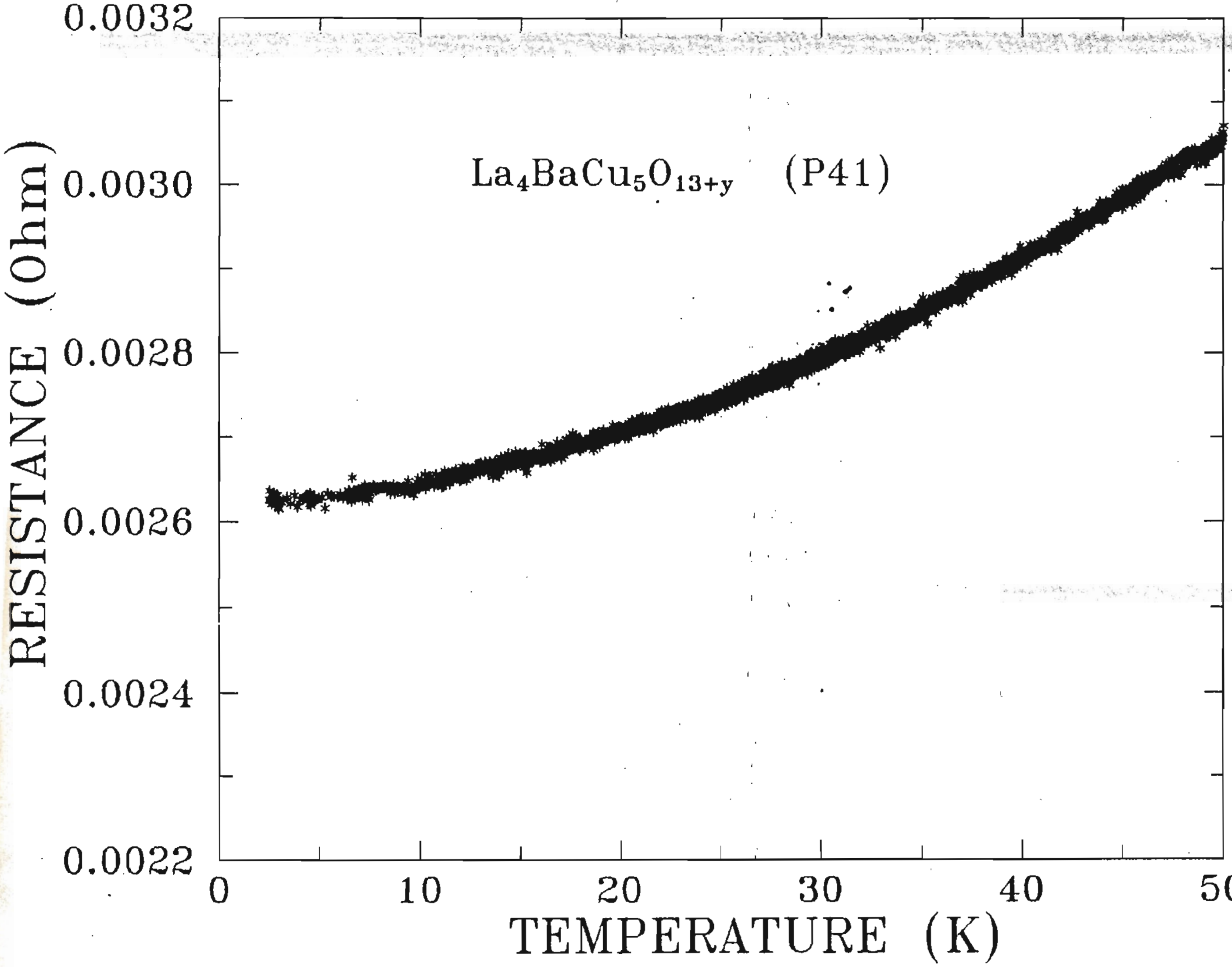
Phys. Rev. B37, 2309 (1988)



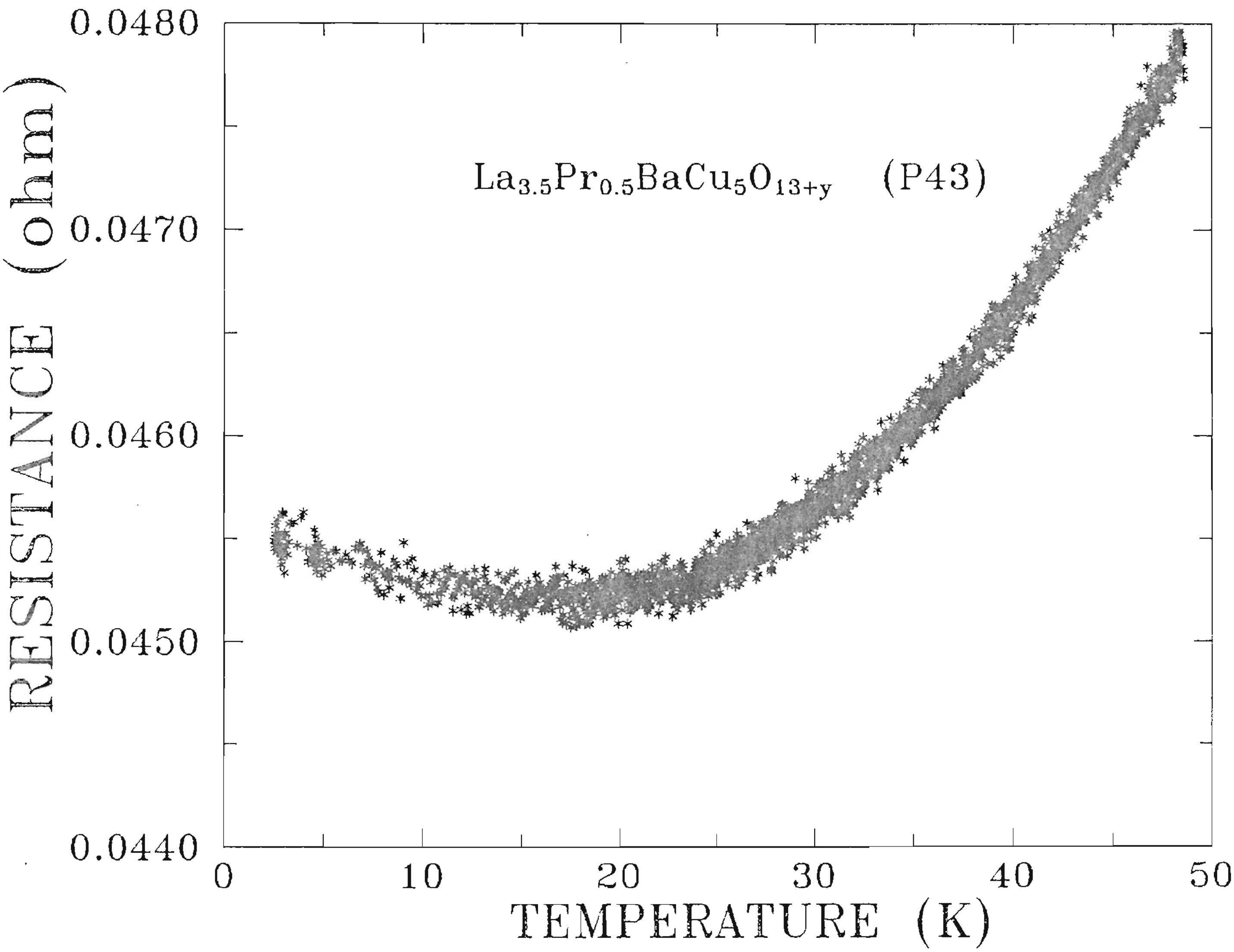


$La_{4-x}Pr_xBaCu_5O_{13\pm\delta}$
x = 0.0
$\rho(T) = \rho_0 + \rho_G(T<\Theta_D) + \alpha T$
ρ_0 = 1.9472 mΩ×cm
α = 0.0168 mΩ×cm/K
Resistivity (mΩ×cm)
Temperature (K)
1
2
3
4
5
6
0
50
100
150
200
250
300

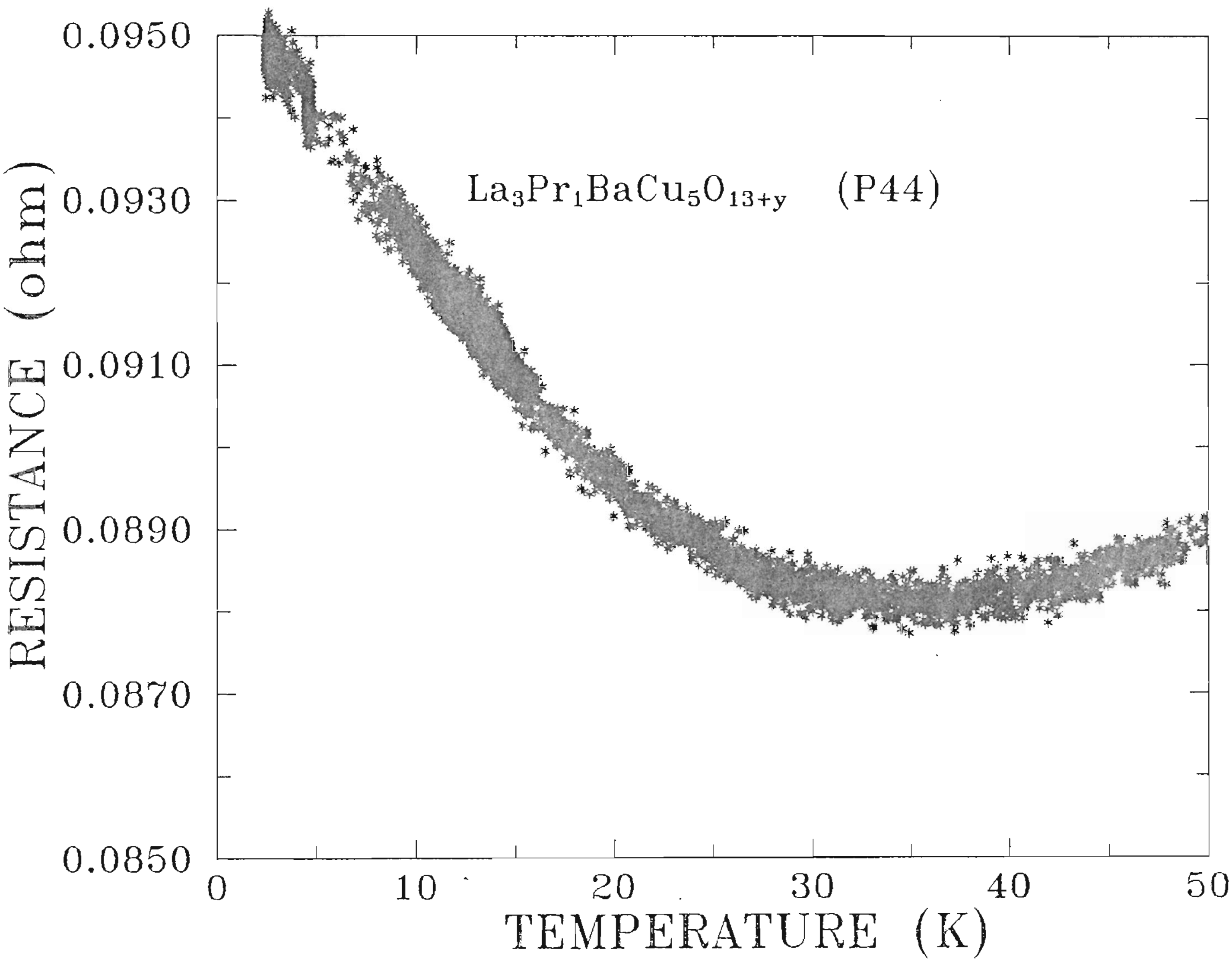

La4-X PrX BaCu5 O13
X=0
X=1.5
X=2
RESISTIVITY (mΩ-cm)
6.0
4.8
3.6
2.4
1.2
0
30
60
90
120
150
180
210
240
270
300
TEMPERATURE (K)



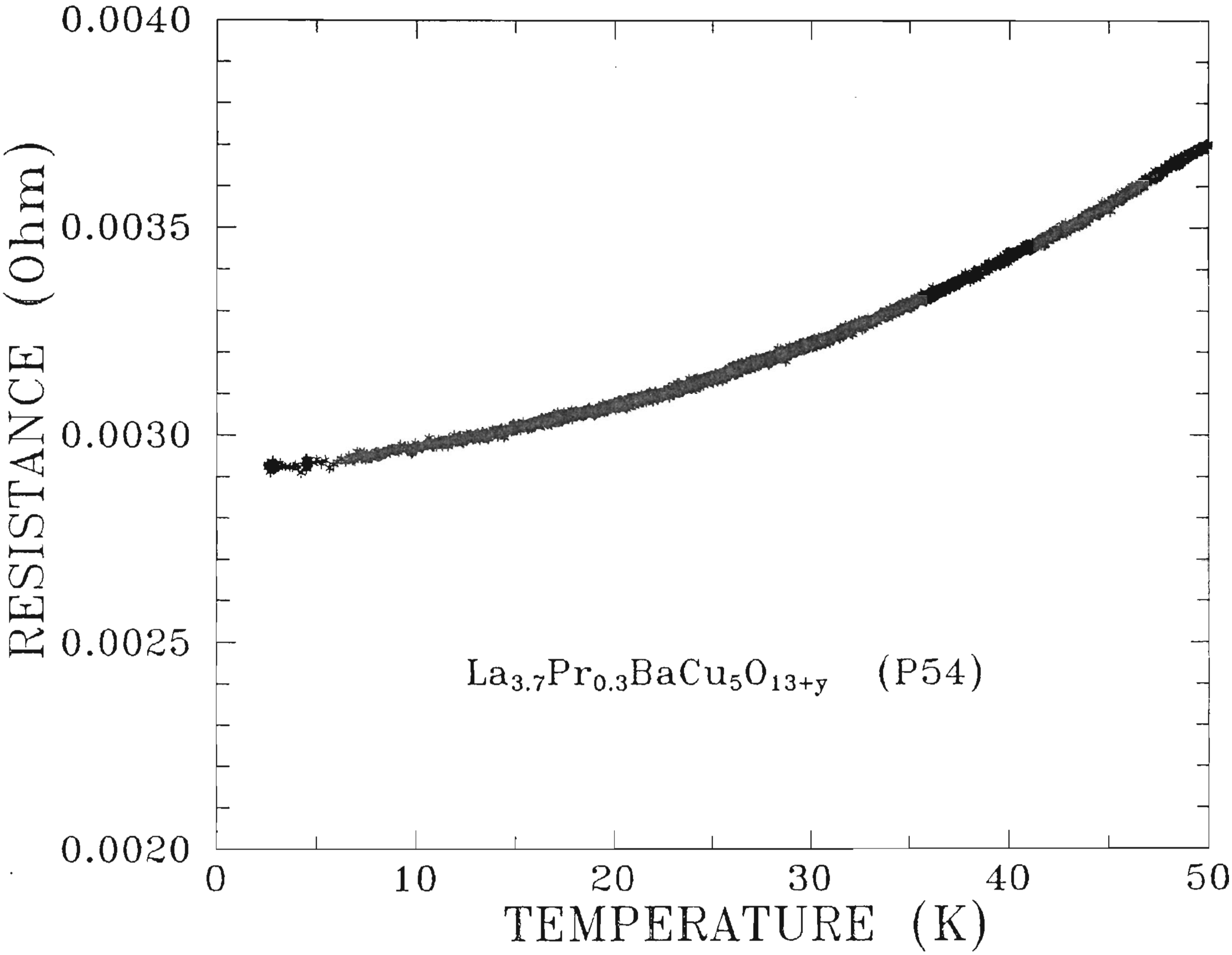
La4BaCu5O13+y (P41)
RESISTANCE (Ohm)
0.0032
0.0030
0.0028
0.0026
0.0024
0.0022
0
10
20
30
40
50
TEMPERATURE (K)



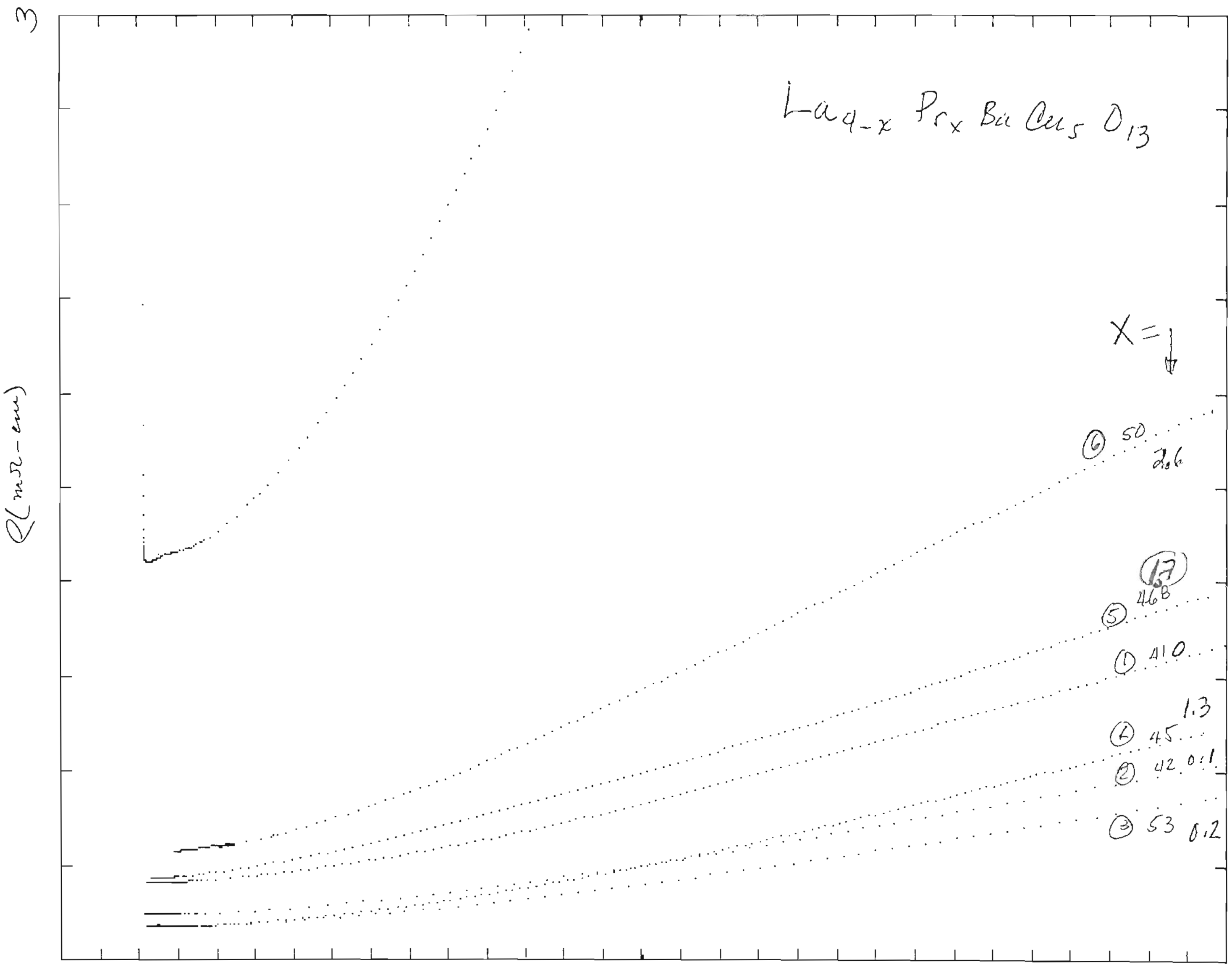
0.0480
0.0470
0.0460
0.0450
0.0440
RESISTANCE (ohm)
$La_{3.5}Pr_{0.5}BaCu_5O_{13+y}$ (P43)
0
10
20
30
40
50
TEMPERATURE (K)

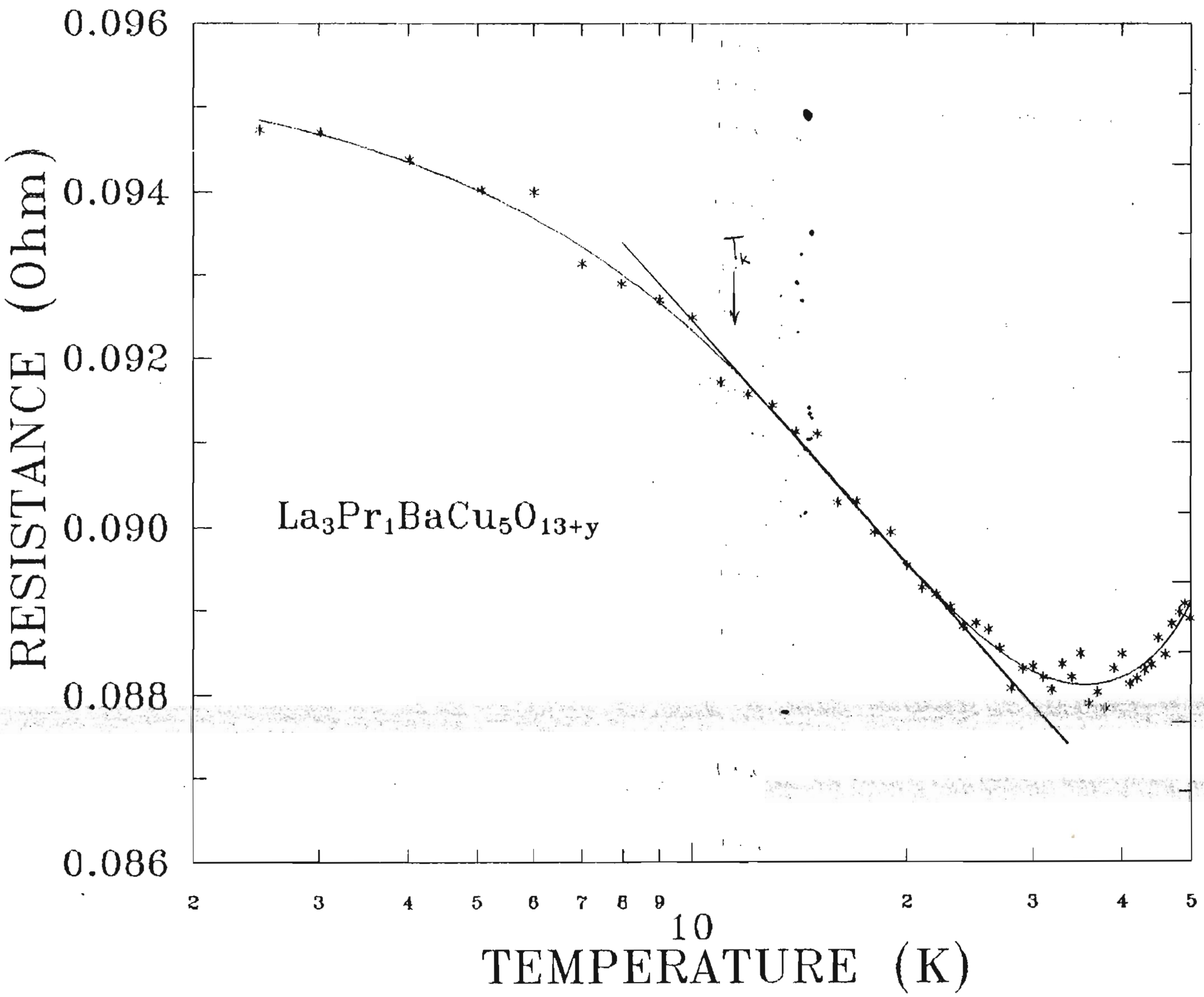


0.0950
0.0930
0.0910
0.0890
0.0870
0.0850
RESISTANCE (ohm)
La3Pr1BaCu5O13+y (P44)
0
10
20
30
40
50
TEMPERATURE (K)

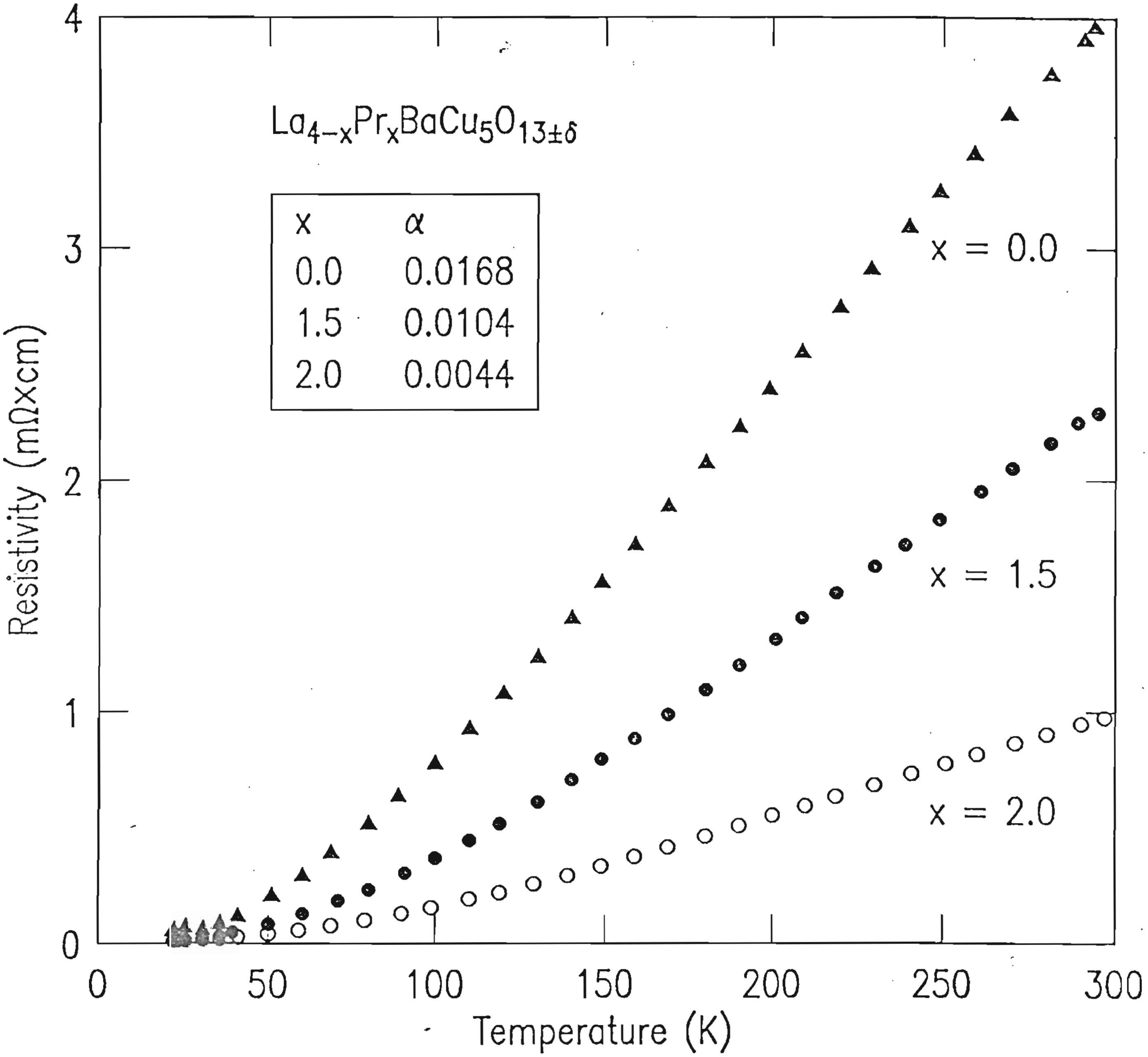


RESISTANCE (Ohm)
0.0040
0.0035
0.0030
0.0025
0.0020
0
10
20
30
40
50
TEMPERATURE (K)
$La_{3.7}Pr_{0.3}BaCu_5O_{13+y}$ (P54)

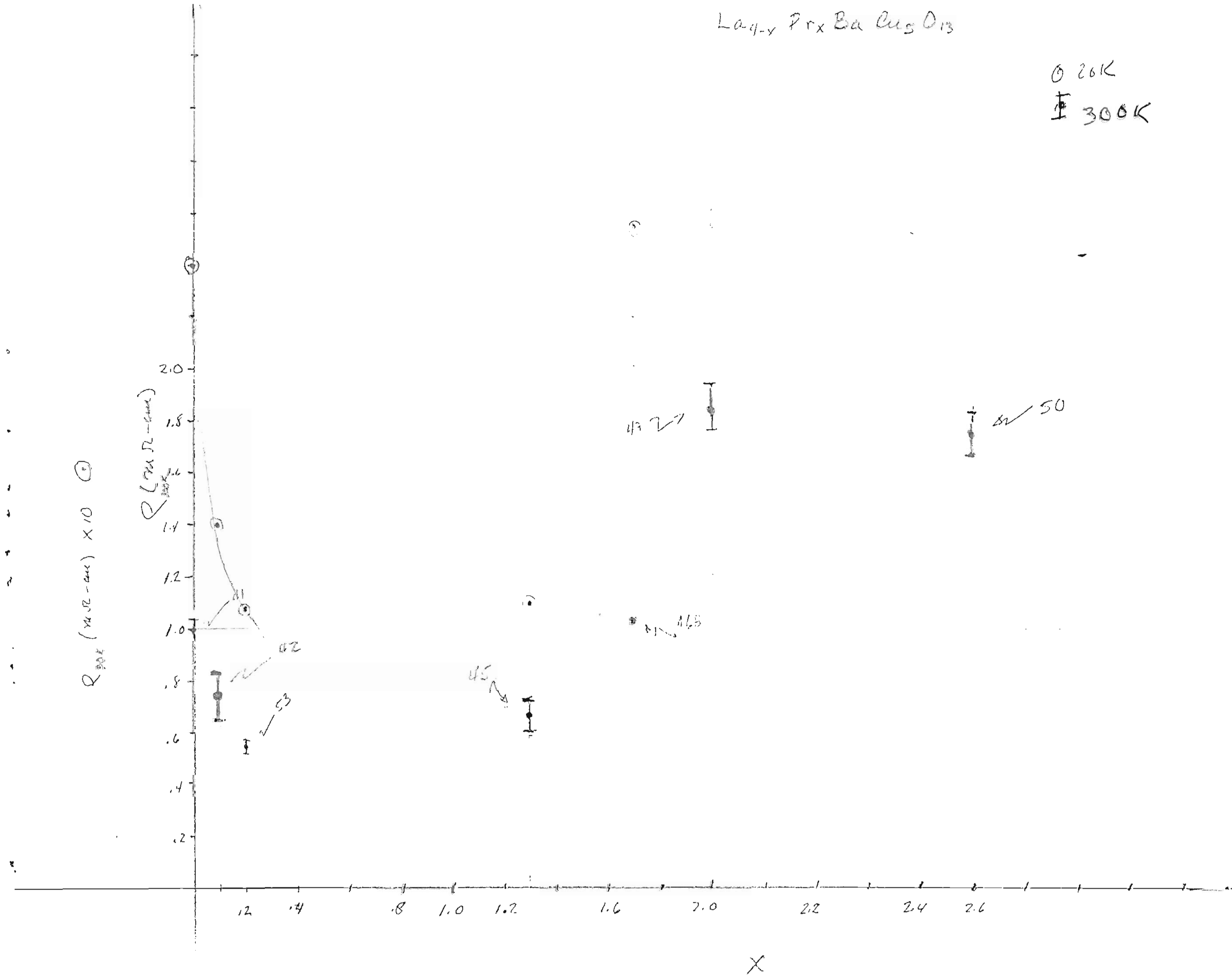

3
$La_{4-x}Pr_xBaCu_5O_{13}$
ρ(mΩ-cm)
X =
⑥ 50
2.6
1.7
⑤ 468
① 410
1.3
④ 45
② 42 0.1
③ 53 0.2


0.096
0.094
0.092
0.090
0.088
0.086
RESISTANCE (Ohm)
T_k
$La_3Pr_1BaCu_5O_{13+y}$
2
3
4
5
6
7
8
9
10
2
3
4
5
TEMPERATURE (K)

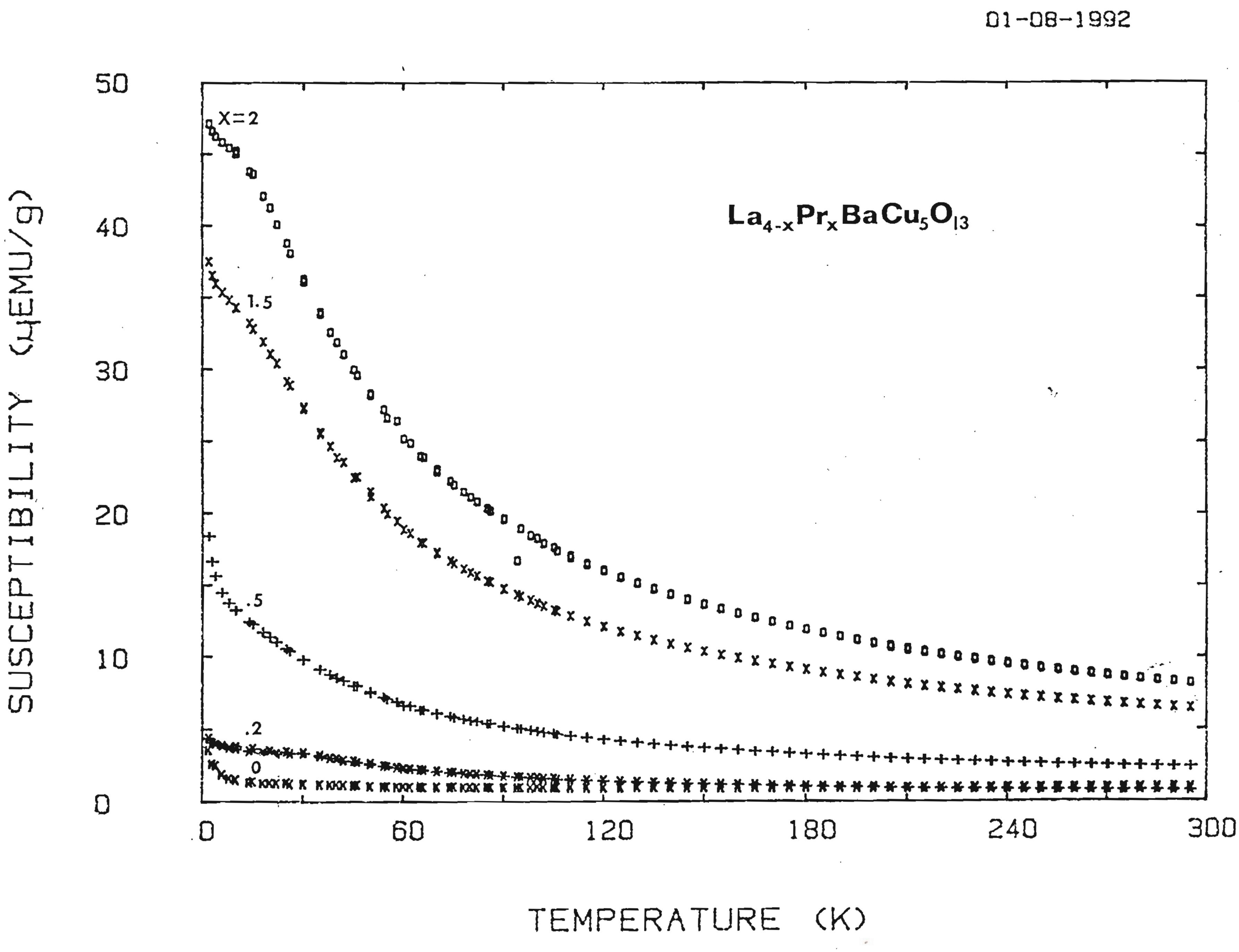
T_k ~ 11.5 K



$La_{4-x}Pr_xBaCu_5O_{13\pm\delta}$
x α
0.0 0.0168
1.5 0.0104
2.0 0.0044
x = 0.0
x = 1.5
x = 2.0
Resistivity (mΩxcm)
Temperature (K)
0
1
2
3
4
0
50
100
150
200
250
300

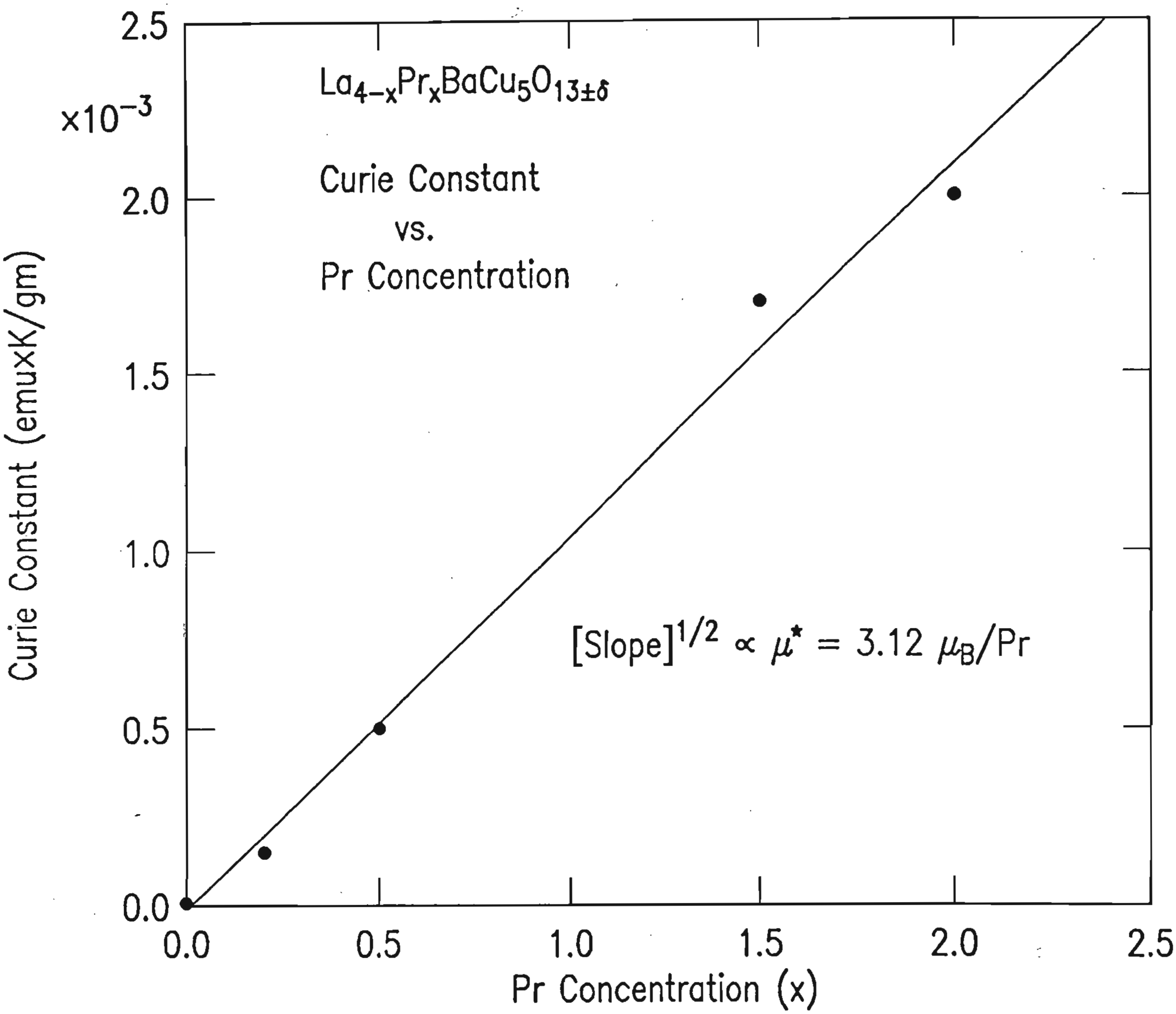


La4-x Prx Ba Cu5 O13
26K
300K
X
2.0
1.8
1.4
1.2
1.0
.8
.6
.4
.2
.2
.4
.8
1.0
1.2
1.6
2.0
2.2
2.4
2.6
53
45
50


01-08-1992
$La_{4-x}Pr_xBaCu_5O_{13}$
X=2
1.5
.5
.2
0
SUSCEPTIBILITY (μEMU/g)
TEMPERATURE (K)
0
10
20
30
40
50
0
60
120
180
240
300

$$\chi = \chi_o + \frac{C}{T - \Theta}$$

$La_{4-x}Pr_xBaCu_5O_{13}$	χ_o (10^{-6} emu/g)	C (emu K/g)	Θ (K)
x=0.0	1.10	8.0 x 10^{-6}	0
x=0.2	0.46	1.5 x 10^{-4}	-12
x=0.5	1.00	5.0 x 10^{-4}	-25
x=1.5	1.40	1.7 x 10^{-3}	-34
x=2.0	2.00	2.0 x 10^{-3}	-20

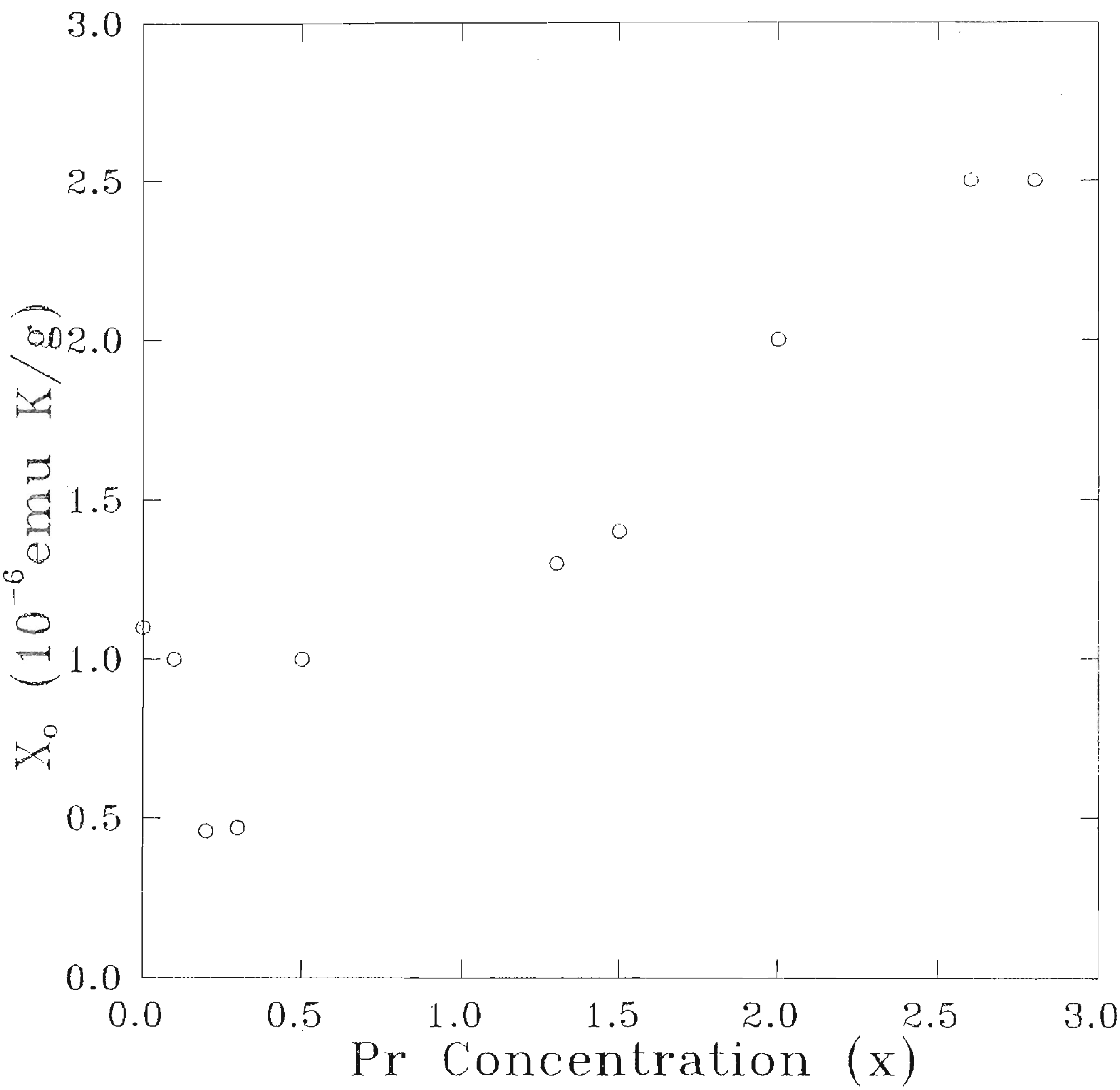


$La_{4-x}Pr_xBaCu_5O_{13\pm\delta}$
Curie Constant
vs.
Pr Concentration
$\times 10^{-3}$
Curie Constant (emu×K/gm)
$[\mathrm{Slope}]^{1/2} \propto \mu^* = 3.12\ \mu_B/\mathrm{Pr}$
Pr Concentration (x)
0.0
0.5
1.0
1.5
2.0
2.5

$$\chi = \chi_o + \frac{C}{T - \Theta}$$

$La_{4-x}Pr_xBaCu_5O_{13}$	χ_o (10^{-6} emu/g)	C (emu K/g)	Θ (K)
x=0.0	1.10	8.0 x 10^{-6}	0
x=0.2	0.46	1.5 x 10^{-4}	-12
x=0.5	1.00	5.0 x 10^{-4}	-25
x=1.5	1.40	1.7 x 10^{-3}	-34
x=2.0	2.00	2.0 x 10^{-3}	-20

$\chi_0 = \mu^2 D(\epsilon_F)$



$La_{4-x}Pr_xBaCu_5O_{13\pm\delta}$ Summary

- "Quasi"-3D metal
- Single phase for $x \leqq 2$
- Pauli χ_0 and TEP suggest E_F independent of x
- Curie constant indicates Pr^{3+} independent of x
- ρ decreases as x increases -- anomalous behavior -- needs further study

$La_{4-x}Pr_xBaCu_5O_{13\pm\delta}$
Future Agenda

- More resistivity and TEP experiments
- Understand why material is only single phase for $x \leqq 2$
- Continuara....

No se pierda el proximo capitulo de su novela favorita,

"Los fisicos tambien lloran"

a la misma hora
y por los mismos actores

Indianapolis APS March Meeting