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Review of Nonstoichiometry in $YBa_2Cu_3O_{7-x}$

Terrence B. Lindemer
Alfred L. Sutton, Jr.

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Chemical Technology Division

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REVIEW OF NONSTOICHIOMETRY IN $YBa_2Cu_3O_{7-x}$

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ABSTRACT

The literature data for the dependence of x in $YBa_2Cu_3O_{7-x}$ on temperature and oxygen pressure was retrieved to provide a numerical data base. These data were reviewed, and each data set was fitted to give the general interrelationship of the experimental variables.

1. INTRODUCTION

There are discrepancies in the literature data for the temperature and oxygen pressure dependence of the nonstoichiometry of $YBa_2Cu_3O_{7-x}$. This compound is often called "123" and is one of the recently discovered superconducting oxides. Also, there is no reported expression relating the interdependence of these experimental variables.

There are two primary objectives in this paper. First, data will be extracted from the literature and will be reviewed in an attempt to determine those data that are consistent among the several authors. Second, chemical thermodynamic representations will be derived to relate the interdependence of the chemical potential of oxygen, hereafter called oxygen potential, on temperature and nonstoichiometry.

2. SYNOPSIS OF PREVIOUS STUDIES

Several thermogravimetric (TGA) studies have been made of the dependence of oxygen per six metals (O/6M) on temperature and oxygen partial pressure. The first authors of the previous studies are Gallagher,[1] Kishio,[2] Specht,[3] Strobel,[4] and Yamaguchi;[5] in addition, Takayama-Muromachi's second article[6,7] gives limited data. Additional work by Marucco et al.[8] and Iwase et al.[9] has been reported but appears

so different from the others that their results were not considered further. Very recent work at 973–1073 K by Tetenbaum et al.[10] was not included in this draft, but apears to be in the middle of the data base.

The experimental details are only briefly summarized here. The same details were sought in each paper, and if some information appears absent, it was not in the original paper. The O/6M data were also obtained. We either extracted all the original data or representative values obtained from the lines drawn by the original authors between their data points. This was done by enlarging the original figures by 300% and reading the numerical values with the aid of a variable rule. The numerical values are given in Appendix 1.

Gallagher. The sample was made from barium carbonate, yttria, and cupric oxide, hereafter called the standard starting materials. The unpelletized mixed powder was calcined in flowing air at 1173 K, milled in acetone to exclude air, pelletized, and sintered at 1223 K. X-ray diffraction (XRD) and microstructural analysis indicated single-phase material. In the TGA, a 100-mg powdered sample was apparently treated either isothermally or at a heating rate of 1 K/min, with a gas flow of 60 mL/min; no initial treatment of the specimen in the TGA was given. In a later paper,[11] the absolute O/6M was determied by reduction in N_2–15% H_2 at 1 K/min to a maximum temperature of 1273 K; this procedure indicated a maximum O/6M of 6.98 ± 0.01. The reduced material contained only baria, yttria, and Cu; they also noted retention of water, probably as hydroxides, at reduction temperatures below 1200 K. We extracted the experimental points from their Fig. 5, and a second set was obtained at 100 K increments from their Fig. 2.

Kishio. Samples were made either by an unspecified powder-mixing method or by coprecipitation from "high purity" nitrate solution in saturated oxalic acid solution. The latter precipitates were calcined in air at 1073 K, ground, and fired in air at 1223 K. No pelletization, which would appear to enhance homogenization, was noted. XRD was used to check the material, but results were not given. The TGA measurements were made on a powder hung in a platinum basket in flowing oxygen/argon mixtures. The absolute values of O/6M were determined on several samples

by iodometric titration, with a maximum O/6M of 6.93 ± 0.02. (Their low-temperature O/6M values seem markedly lower that those of all other data sets at equivalent conditions.) We extracted the experimental values shown in their Fig. 1.

Specht. Samples were made from the standard materials, which were at least 99.997% pure and which were preheated before mixing. After this pretreatment, all sample preparations were performed in a helium glove box with <2 ppm carbon dioxide, water, and oxygen. The sample was mixed, pelletized, and calcined to 1173–1193 K in oxygen, followed by two repetitions of grinding, pelletizing, and firing to 1213–1223 K. The work of Specht et al.[3] also included a high-temperature XRD study. Since the authors did not mention the presence of second phases, it was assumed here to be single-phase material. The TGA measurements were unique in that subatmospheric oxygen pressures were established by evacuation. No initial treatment in the TGA was given. Absolute O/6M values were determined by reducing in pure hydrogen at 923 K; baria, yttria, and copper were assumed as final products. A sample cooled slowly in one atm of oxygen gave O/6M = 6.97 ± 0.02. The O/6M data were extracted from a large plot provided by the authors.

Strobel. The sample was made from the standard materials of >99.9% purity. It was fired at 1220 K in air or oxygen, with itermediate ball-milling. No pelletization, which would appear to enhance homogenization, was noted. A sample of unspecified weight was suspended in a silica crucible in the TGA; platinum was avoided because it reacted at 1170 K and low oxygen pressure. The initial condition in the TGA was 600 K in oxygen. Flows of 1 to 2 L/h of oxygen, air, and air-argon were used. The maximum O/6M was 7 from neutron diffraction, which was also used to indicate a single-phase material. We extracted the data points from Fig. 1, with Fig. 2 being used to verify the experimental temperatures, which were rather confusing in Fig. 1.

Takayama-Muromachi. The sample was made from the standard materials at 1203 K with no atmosphere stated and using intermediate grindings, giving a 7-g sample. No pelletization, which would appear to improve homogenization, was noted. XRD indicated only "123" material. In the

TGA, no initial condition was given; air was used except for the use of oxygen at 641 K. The absolute O/6M was estimated to be 7.0 based on hydrogen reduction at 1173 K; reduction at 923 K led to water retention, with barium hydroxide being suggested. Inert gas fusion gave 6.7, while an unspecified analysis gave 6.89. We extracted the O/6M data from their Fig. 1.

Yamaguchi. The sample was made from "high-purity" barium carbonate, yttria, and copper metal in oxygen at 1203 K, with two or three intermediate grindings. XRD indicated single-phase material. The sample was pressed into a 10- by 1-mm pellet that weighed 500 mg and was sintered at 1223 K. It was suspended with Pt in the TGA and was initially heated to 873 K, but no atmospheric composition was given. The absolute O/6M was determined on a pellet slowly cooled to ambient in oxygen, then reduced at 2973 K, giving 6.95 to 7.01; they assumed treatment at 473 K in oxygen gave 7.00, which was consistent with log(x) vs $\log(p^*_{O_2})$ being linear at low x. We extracted data from Figs. 1 and 2 to give independent sets.

3. CHEMICAL THERMODYNAMIC REPRESENTATIONS

There are a number of objectives in developing a chemical thermodynamic representation of the nonstoichiometry of the "123" compound. The data indicate that the chemical formula can be written as $YBa_2Cu_3O_{7-x}$, with $0<x<1$. One objective is an accurate representation of the slope of the experimental $\ln(x)$-$\ln(p^*_{O_2})$ data as x approaches zero; here $p^*_{O_2}$ is the oxygen pressure in MPa divided by the standard-state pressure, 0.101 MPa. A plot of these variables is commonly used for nonstoichiometric systems and the slope usually approaches a constant value as x becomes small. At small values of x, the representation to be developed here reduces to the simple expression

$$\ln(p^*_{O_2}) = a/T + b - s_1 \ln(x) \quad . \tag{1}$$

A second objective is the analogous representation of the $\ln(1-x)$-$\ln(p^*_{O_2})$ data as x approaches unity, which will reduce to the simple expression

$$\ln(p^*_{O_2}) = c/T + d + s_2 \ln(1-x) \quad . \tag{2}$$

Here, T is temperature in kelvin, a, b, c, and d are constants, s_1 is the absolute value of the slope of the isothermal $\ln(p^*_{O_2}) - \ln(x)$ plot as $x \to 0$, and s_2 is similarly defined as $(1-x) \to 0$. The general approach has been developed at ORNL for other nonstoichiometric oxides,[12-18] and will thus be described here in abbreviated fashion.

Several considerations lead to the final representation. The starting point is a chemical equilibrium involving oxygen and, in the present case, two "mass parameters" that are analogous to chemical species in a solid solution, the only difference being that mass parameters may be composed of noninteger numbers of atoms. For the present system, the experimental O/6M data permit one to write two independent mass-balance equations, one for the total mols of oxygen (7-x) and one for the total mols of metal (6), and thus the mols of two independent mass parameters may be determined. Since the O/6M values range from 6 to 7, this can be achieved by assuming that one of mass parameters has an O/6M of 6 and the second mass parameter has an O/6M of 7. These considerations lead to the equilibrium to be used here,

$$s_1\ Y_{2/s_1}Ba_{4/s_1}Cu_{6/s_1}O_{12/s_1} + O_2 = s_2\ Y_{2/s_2}Ba_{4/s_2}Cu_{6/s_2}O_{14/s_2}\ , \qquad (3)$$

which is abbreviated to

$$s_1\ M_{12/s_1}O_{12/s_1} + O_2 = s_2\ M_{12/s_2}O_{14/s_2}\ . \qquad (4)$$

The left-hand mass parameter has the oxygen-to-metal ratio at x = 1, i.e., O/6M = 6, and the right-hand one that for x = 0, where O/6M = 7. The mols of each are designated as m_1 and m_2, respectively, and are calculated from the mass-balance equations for the metals

$$6 = (12/s_1)\ m_1 + (12/s_2)\ m_2 \qquad (5)$$

and for oxygen

$$7 - x = (12/s_1)\ m_1 + (14/s_2)\ m_2\ . \qquad (6)$$

Upon solving for the mols, one obtains

$$m_1 = 0.5\ s_1\ x \qquad (7)$$

and

$$m_2 = 0.5\ s_2\ (1-x)\ . \tag{8}$$

These values are used to calculate the mol fractions N_1 and N_2. The equilibrium constant for the equilibrium of Eq. (4) leads to

$$RT\ \ln(p^*_{O_2})\ (\mathrm{J/mol}) = \Delta H^o_{rxn} - T\Delta S^o_{rxn} + s_2\ RT\ \ln(N_2) - s_1\ RT\ \ln(N_1) \tag{9}$$

in which R is the gas constant, ΔH^o_{rxn} is the standard enthalpy for the equilibrium, and ΔS^o_{rxn} is the standard entropy. This equation was used in a least-squares fit of the experimental data for each crystalline structure of the "123" compound, and gave the values of the enthalpy, entropy, s_1, and s_2. To do this, a linear least-squares method was used to iterate over several assumed values of s_1 and s_2, with the enthalpy and entropy terms being determined at a given value of s_1 and s_2, and with the best fit being that with the smallest residuals. The resulting values for each study are given in Table 1.

Table 1. Fitted values for Eq. (9)

First author	s_1	s_2	ΔH^o_{rxn} (J/mol)	ΔS^o_{rxn} ($J \cdot mol^{-1} \cdot K^{-1}$)
		Orthorhombic phase		
Gallagher	4.0	3.5	-225300	-213.4
Kishio[a]	5.0	2.0	-209800	-206.5
Specht	2.5	3.0	-160700	-152.8
Strobel	6.0	2.0	-151800	-147.3
Yamaguchi	3.0	2.5	-167000	-166.8
		Tetragonal phase		
Gallagher	6.0	3.0	-205300	-196.1
Kishio	4.0	3.0	-185700	-173.9
Specht	6.0	2.0	-146300	-144.6
Strobel	2.5	2.0	-163100	-157.5
Yamaguchi	5.0	2.5	-168100	-170.2

[a]Data below 500°C were not fitted because the O/6M values approach 6.93 instead of 7.

It should be noted that for all the data sets the conditions for the orthorbombic-to-tetragonal transition were obtained from Specht et al.[3] The value of x at the transition, x_{tr}, can be approximated by

$$x_{tr} = [1 + \exp(2.409 - 1636T_{tr}^{-1})]^{-1} \tag{10}$$

in which T_{tr} is the transition temperature in kelvin. As with most oxide-oxide-oxygen equilibria, the oxygen potential for the transition should be nearly linear with temperature, which leads to

$$\log_{10} (p^*_{O_2,tr}) = 11.53 - 10929\ T_{tr}^{-1}\ . \tag{11}$$

4. DISCUSSION

Some of the literature data are compared in Figs. 1 and 2. Data near 773 K and 1073 K are plotted in Fig. 1, and the results of Specht et al.,[3] Strobel et al.[4] (at 813 K and 1065 K), and Yamaguchi et al.[5] exhibit similar behavior. The 773 K data of Kishio et al.[2] and Gallagher et al.[1] clearly deviate from the rest. In Fig. 2, data at $p^*_{O_2}$ = 1 and 0.01 are plotted. The abcissa for this figure results from m_1=m_2=2, Eqs. (7) and (8), and is a convenient way to plot data and fits of data because it illustrates the usual Henrian linear behavior as O/6M approaches 6 or 7. This plot clearly demonstrates the deviation of the data of Kishio et al. resulting from their limiting O/6M value of 6.93. In both Figs. 1 and 2, the data of Yamaguchi et al.[5] are displaced somewhat for no apparent reason, but Fig. 2 demonstrates that an error in specimen temperature at a given x could be one explanation. It is also apparent from Fig. 2 that the data disagree more as $p^*_{O_2}$ is lowered, which suggests that equilibrium may be more difficult to establish at these lower values.

Selection of the best data sets is difficult, but the data of Specht et al.[3] and Strobel et al.[4] are the most consistent with one another over the entire experimental range of variables. Preliminary experimental results from an investigation to be reported later[19] are also in best agreement with these two studies.

The parameters given in Table 1 were used to calculate the fitted behavior for each literature study. These results are given with the

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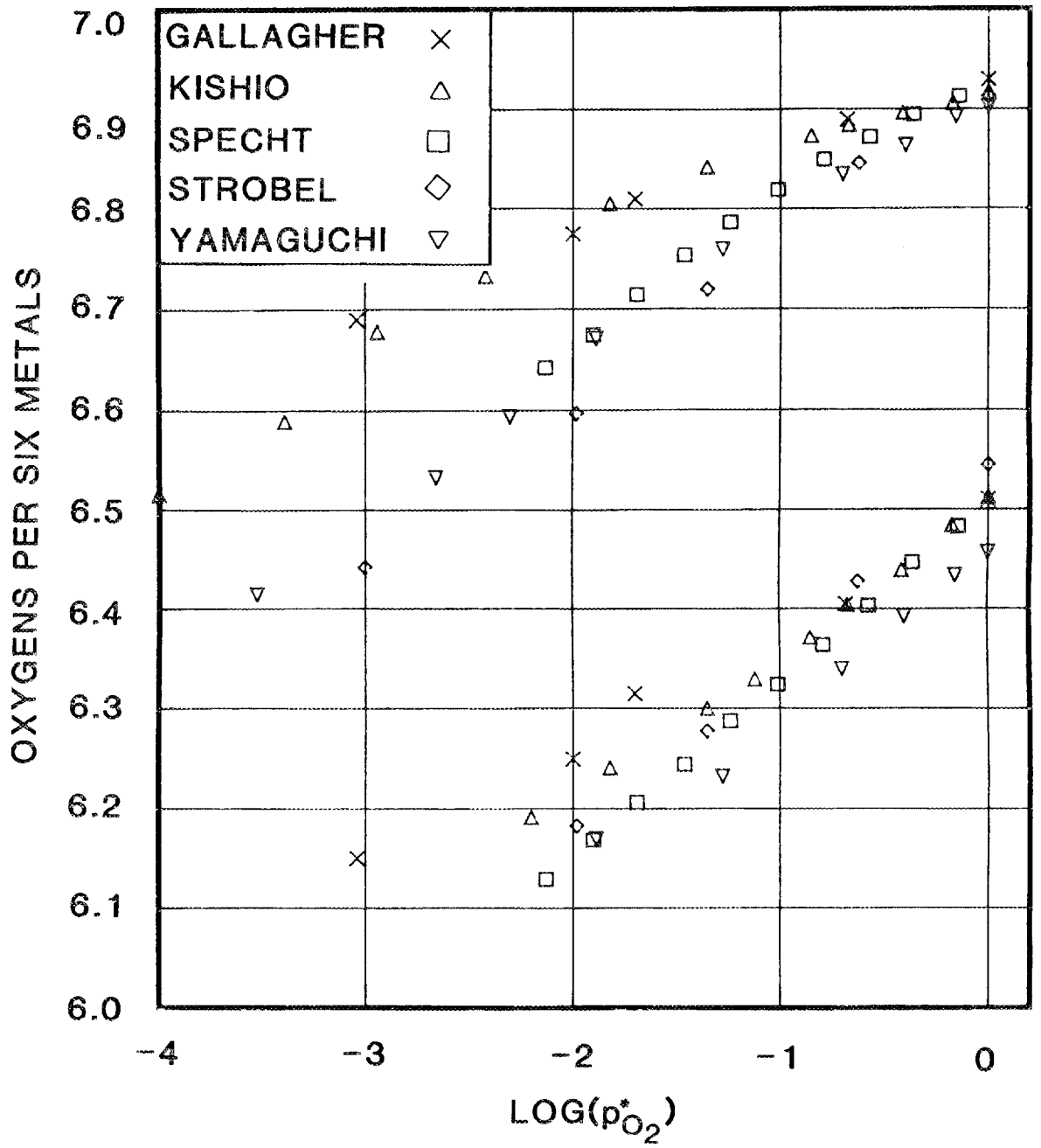

Fig. 1. Comparison of investigations of nonstoichiometry in the "123" compound near 773 (upper data set) and 1073 K, with the exception of Strobel et al., which is at 813 and 1065 K.

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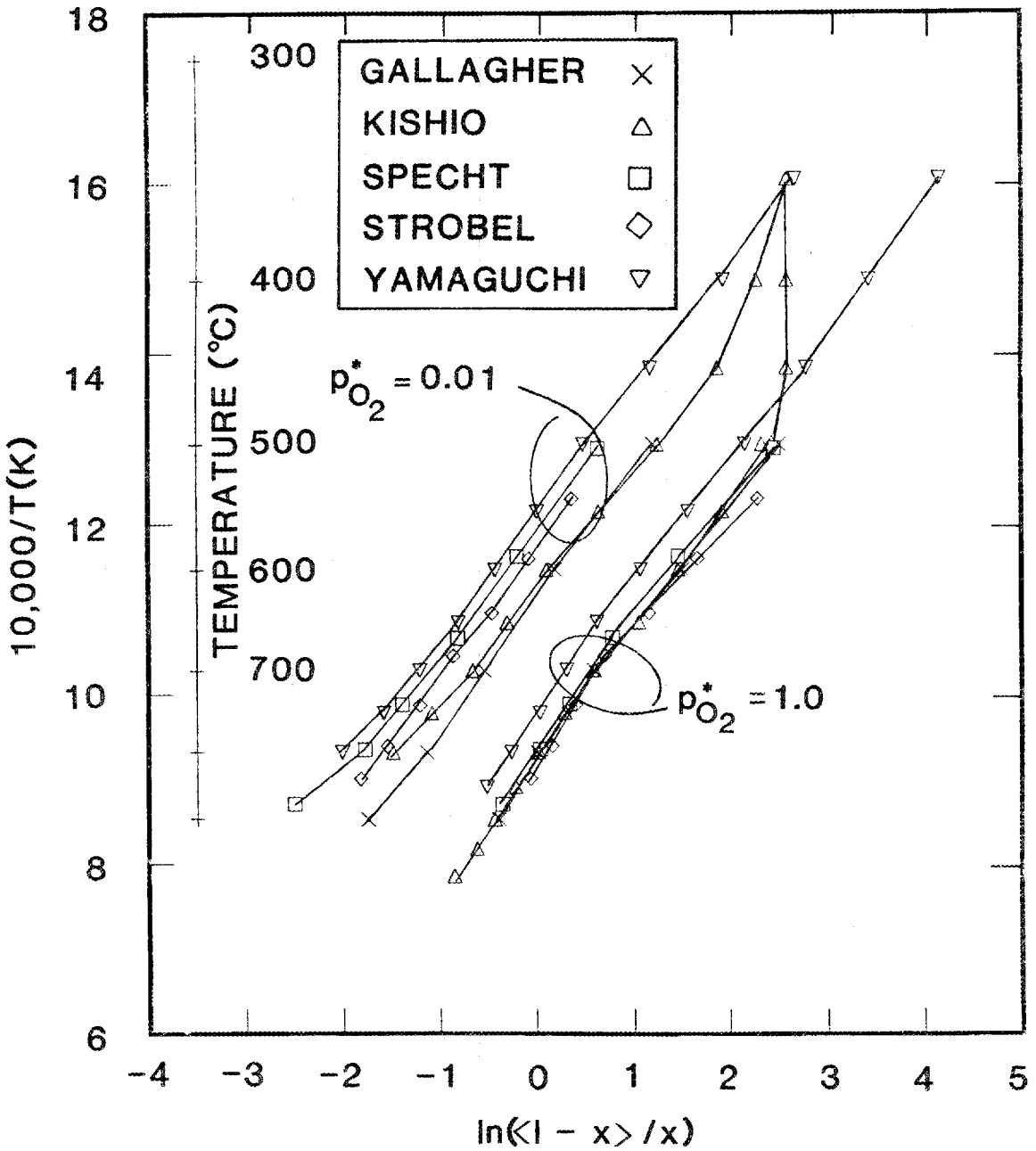

Fig. 2. Comparison of literature data at $p^*_{O_2}$ values of 1 and 0.01.

experimental data in Figs. 3 to 7. Copies of these figures can be superimposed over a light box to further illustrate the similarities and differences of the data sets.

The partial molal enthalpy and entropy of oxygen at given O/6M values are also useful for comparison purposes. The partial molal enthalpy of oxygen, $\Delta\overline{H}(O_2)$, is ΔH^o_{rxn} given in Table 1 for Eq. (9). The partial molar entropy of oxygen at a given O/6M is $\Delta S^o_{rxn} - s_2R\ \ln(N_2) + s_1R\ \ln(N_1)$, as can be seen from Eq. (9). These values are given in Table 2. Thus, at a given O/6M,

$$RT\ \ln(p^*_{O_2})\ (J/mol) = \Delta H^o_{rxn} - T\Delta\overline{S}(O_2)\ . \qquad (12)$$

Table 2. Partial molal entropy of oxygen, Eq. (12)

	First author				
	Gallagher	Kishio	Specht	Strobel	Yamaguchi
O/6M			($J \cdot mol^{-1} \cdot K^{-1}$)		
			Orthorhombic phase		
6.997	-402.1	-410.0	-277.3	-382.4	-307.1
6.990	-361.8	-360.0	-252.1	-322.7	-276.9
6.900	-282.5	-265.9	-201.9	-211.7	-217.6
6.800	-256.1	-238.1	-184.6	-180.3	-197.9
6.700	-238.8	-221.8	-172.9	-162.3	-185.1
6.600	-224.8	-209.7	-163.2	-149.3	-174.8
6.500	-212.1	-199.7	-154.1	-138.6	-165.5
6.400	-199.6	-190.4	-144.8	-129.0	-156.4
			Tetragonal phase		
6.700	-219.2	-196.3	-159.6	-172.3	-189.5
6.600	-202.9	-183.1	-146.6	-163.8	-175.9
6.500	-188.9	-171.4	-135.9	-156.2	-164.2
6.400	-175.9	-160.0	-126.3	-148.8	-153.3
6.300	-162.5	-147.9	-116.7	-140.9	-142.2
6.200	-147.2	-133.6	-105.9	-131.5	-129.4
6.100	-125.4	-112.6	-91.0	-117.6	-111.2
6.030	-92.5	-80.2	-68.9	-96.1	-83.9
6.010	-64.3	-52.2	-50.0	-77.4	-60.4

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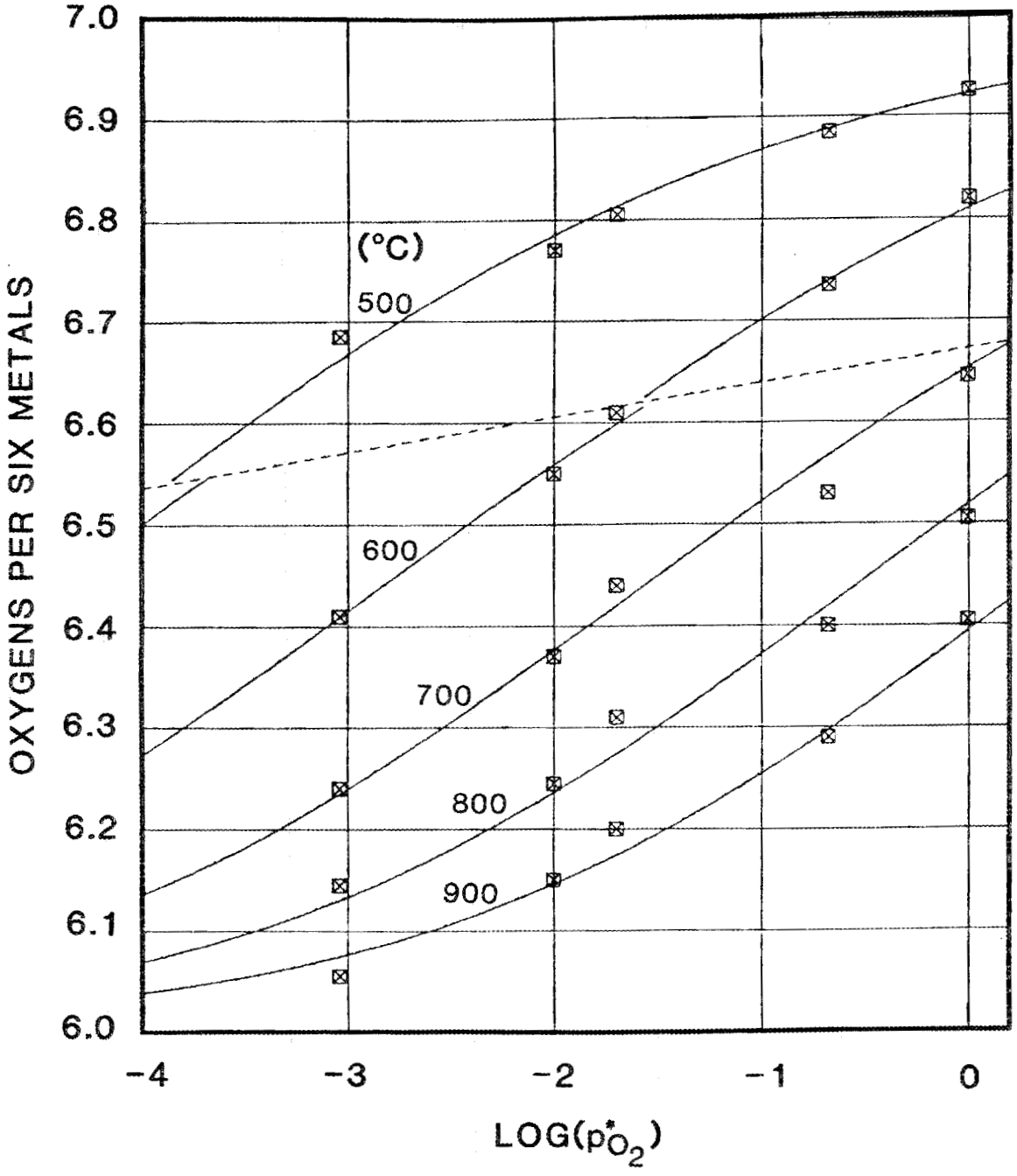

Fig. 3. Data of Gallagher et al. along with fitted behavior, Eq. (9) and Table 1, at the original experimental temperatures. The dashed line is the orthorhombic-to-tetragonal transition from Specht et al.[3]

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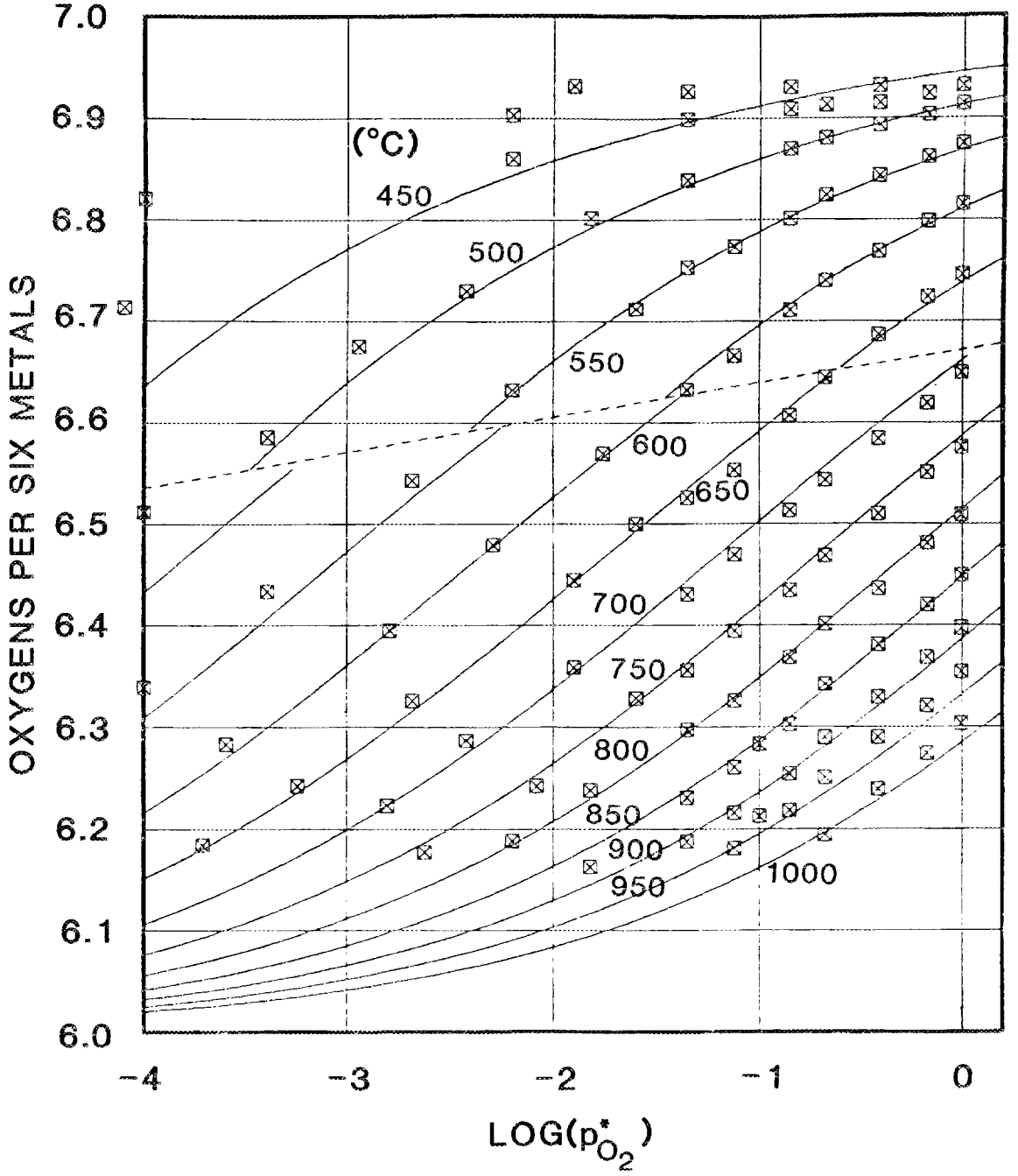

Fig. 4. Data of Kishio et al. along with fitted behavior, Eq. (9) and Table 1, at the original experimental temperatures.

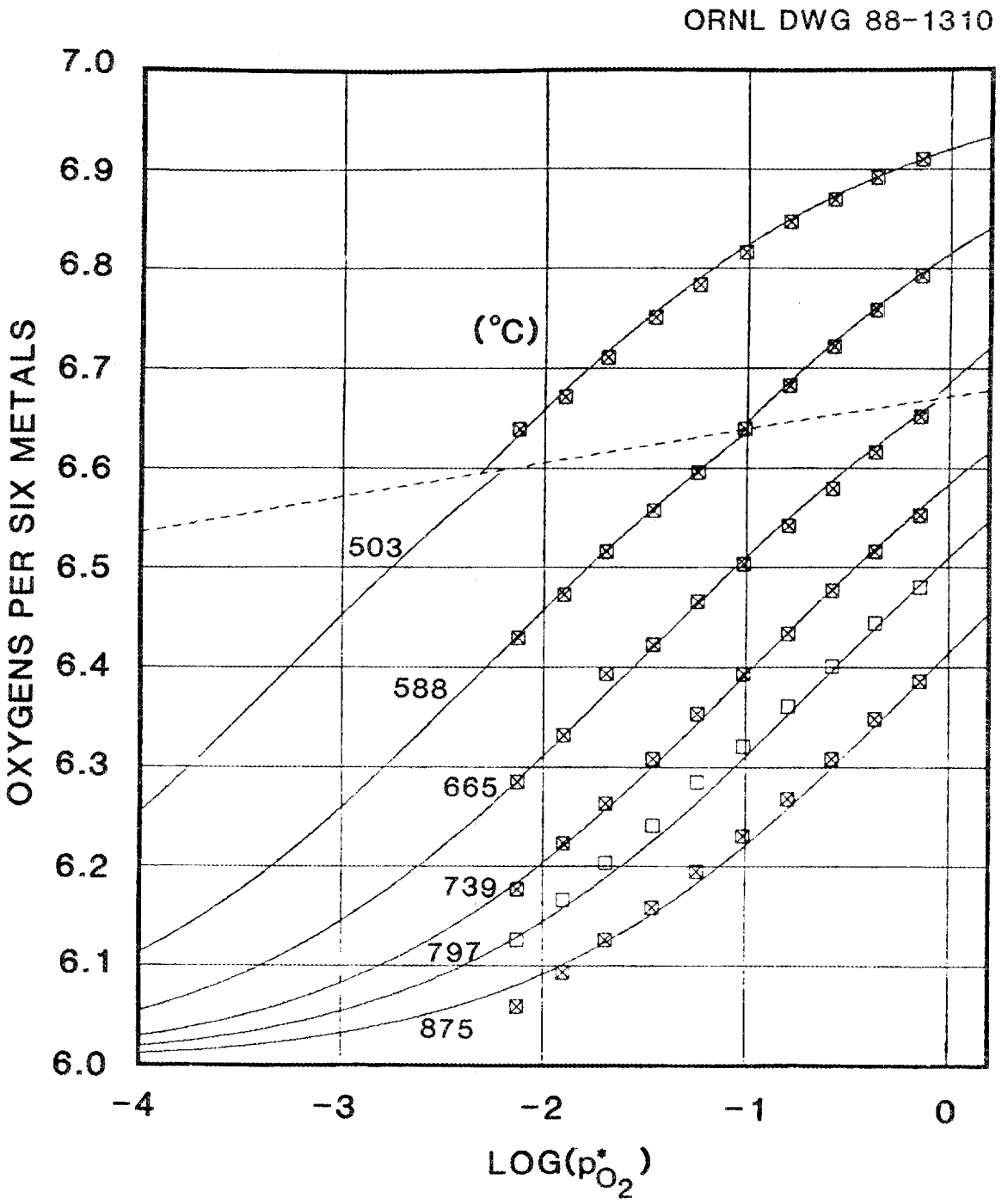

Fig. 5. Data of Specht et al. along with fitted behavior, Eq. (9) and Table 1, at the original experimental temperatures.

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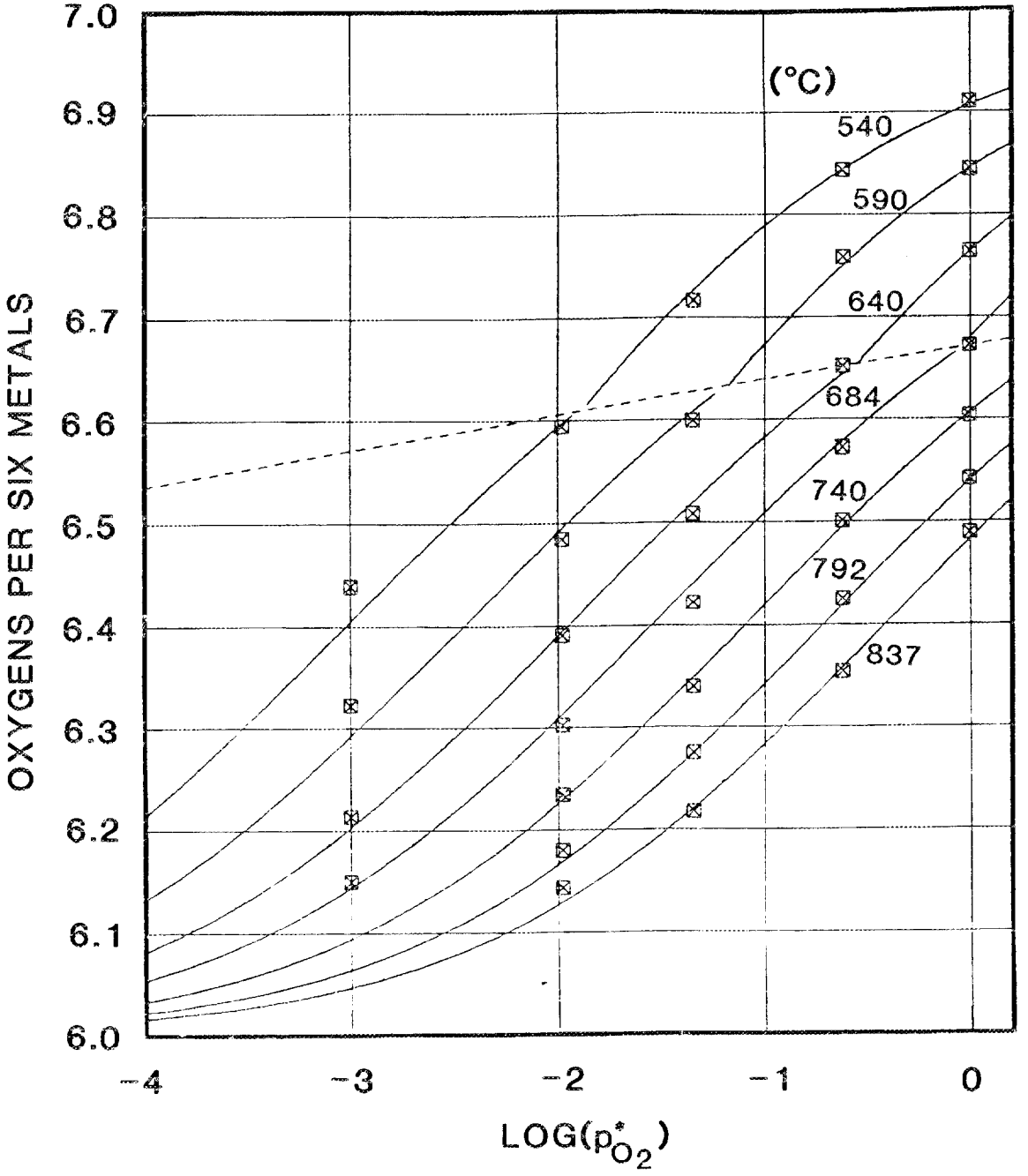

Fig. 6. Data of Strobel et al. along with fitted behavior, Eq. (9) and Table 1, at the original experimental temperatures.

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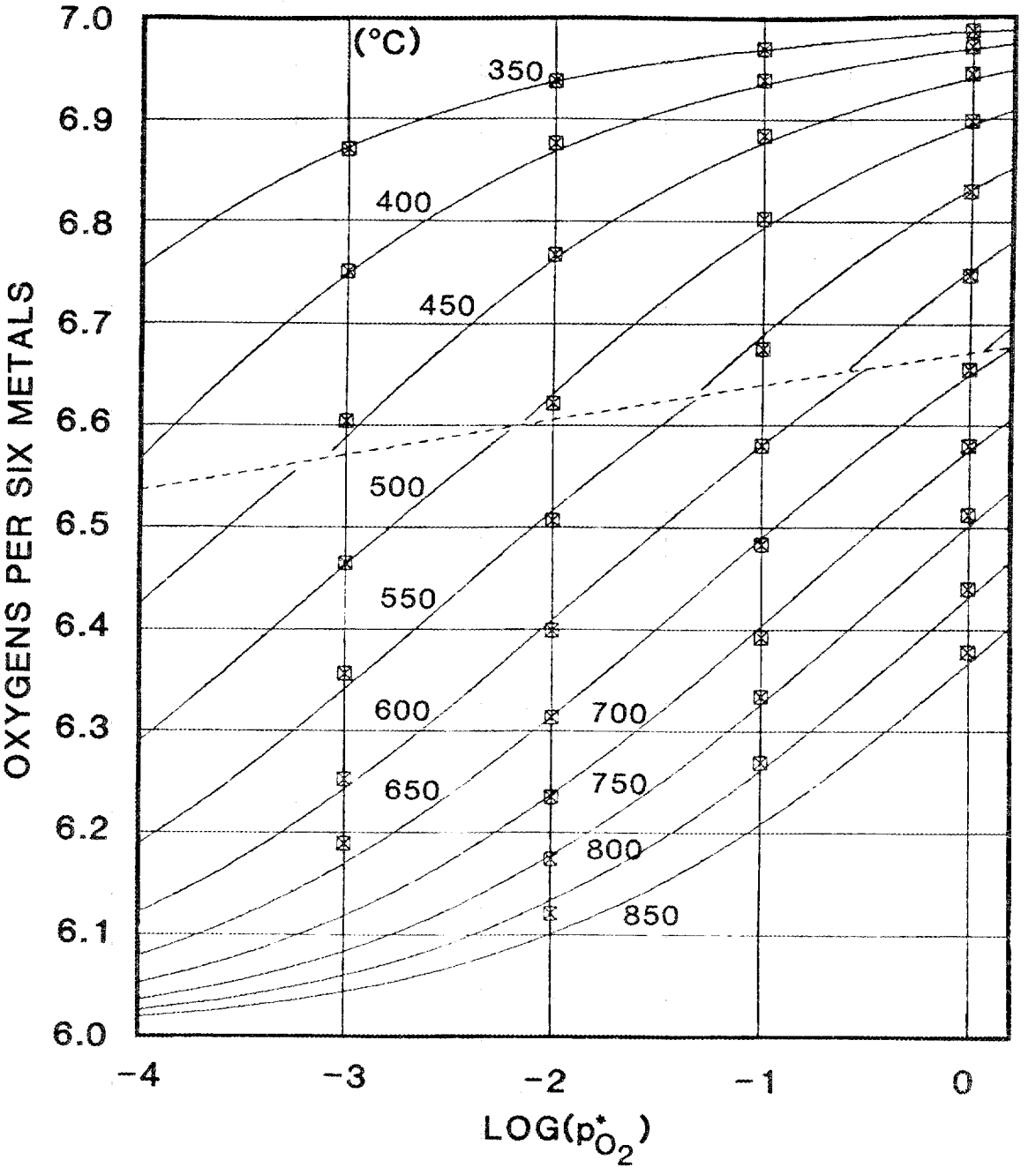

Fig. 7. Data of Yamaguchi et al. along with fitted behavior, Eq. (9) and Table 1, at the original experimental temperatures.

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APPENDIX 1
DATA BASE FOR NONSTOICHIOMETRY IN $YBa_2Cu_3O_{7-x}$

APPENDIX 1. DATA BASE FOR NONSTOICHIOMETRY IN $YBa_2Cu_3O_{7-x}$

Gallagher, Adv. Ceram. Mater. 2 (3B), 632, 1987, Fig. 5

947	-2.0000	6.1000[a]
857	-3.0400	6.1000
899	-1.7000	6.2000
844	-2.0000	6.2000
742	-3.0400	6.2000
897	-0.6700	6.3000
808	-1.7000	6.3000
753	-2.0000	6.3000
315	-3.0400	6.3000
903	0.0000	6.4000
802	-0.6700	6.4000
727	-1.7000	6.4000
679	-2.0000	6.4000
608	-3.0400	6.4000
797	0.0000	6.5000
722	-0.6700	6.5000
653	-1.7000	6.5000
624	-2.0000	6.5000
557	-3.0400	6.5000
717	0.0000	6.6000
657	-0.6700	6.6000
597	-1.7000	6.6000
572	-2.0000	6.6000
523	-3.0400	6.6000
663	0.0000	6.7000
612	-0.6700	6.7000
547	-1.7000	6.7000
527	-2.0000	6.7000
493	-3.0400	6.7000
600	0.0000	6.8000
553	-0.6700	6.8000
496	-1.7000	6.8000
482	-2.0000	6.8000
465	-3.0400	6.8000
516	0.0000	6.9000
485	-0.6700	6.9000
434	-1.7000	6.9000
424	-2.0000	6.9000
417	-3.0400	6.9000

Gallagher, Adv. Ceram. Mater. 2 (3B) 632, 1987, Fig. 2

900	-3.04	6.055
900	-2.00	6.15
900	-1.70	6.20
900	-0.678	6.29
900	0	6.405
800	-3.04	6.145
800	-2.00	6.245
800	-1.70	6.310
800	-0.678	6.4
800	0	6.505
700	-3.04	6.24
700	-2.00	6.37
700	-1.7	6.44
700	-0.678	6.53
700	0	6.645
600	-3.04	6.41
600	-2.00	6.55
600	-1.7	6.61
600	-0.678	6.735
600	0	6.82
500	-3.04	6.685
500	-2.00	6.77
500	-1.70	6.805
500	-0.678	6.885
500	0	6.925

Kishio, Japn. J. App. Phys. 26 L1228-30, 1987, Fig. 1

1000	0	6.301
1000	-0.17	6.272
1000	-0.41	6.237
1000	-0.67	6.192
950	0	6.352
950	-0.17	6.319
950	-0.41	6.288
950	-0.67	6.249
950	-0.85	6.216
950	-1.00	6.210
950	-1.12	6.179
900	0	6.395
900	-0.17	6.366
900	-0.41	6.327
900	-0.67	6.288
900	-0.85	6.252
900	-1.12	6.214
900	-1.35	6.185

[a]These numbers are, respectively, temperature in Celsius, $\log_{10}(P^*_{O_2})$, and O/6M.

850	0	6.447
850	-0.17	6.418
850	-0.41	6.379
850	-0.67	6.340
850	-0.85	6.300
850	-1.00	6.281
850	-1.12	6.259
850	-1.35	6.229
850	-1.82	6.160
800	0	6.507
800	-0.17	6.479
800	-0.41	6.434
800	-0.67	6.399
800	-0.85	6.366
800	-1.12	6.324
800	-1.35	6.295
800	-1.82	6.236
800	-2.20	6.186
750	0	6.574
750	-0.17	6.549
750	-0.41	6.508
750	-0.67	6.466
750	-0.85	6.432
750	-1.12	6.392
750	-1.35	6.354
750	-1.60	6.326
750	-2.08	6.240
750	-2.62	6.175
700	0	6.647
700	-0.17	6.617
700	-0.41	6.582
700	-0.67	6.541
700	-0.85	6.511
700	-1.12	6.467
700	-1.35	6.428
700	-1.90	6.356
700	-2.42	6.285
700	-2.80	6.221
650	0	6.744
650	-0.17	6.722
650	-0.41	6.685
650	-0.67	6.642
650	-0.85	6.605
650	-1.12	6.551
650	-1.35	6.524
650	-1.60	6.498
650	-1.90	6.442
650	-2.68	6.324
650	-3.24	6.240
650	-3.71	6.182
600	0	6.813
600	-0.17	6.796
600	-0.41	6.767
600	-0.67	6.738
600	-0.85	6.709
600	-1.12	6.664
600	-1.35	6.630
600	-1.76	6.568
600	-2.29	6.477
600	-2.79	6.393
600	-3.59	6.281
550	0	6.873
550	-0.17	6.860
550	-0.41	6.841
550	-0.67	6.822
550	-0.85	6.799
550	-1.12	6.771
550	-1.35	6.751
550	-1.60	6.710
550	-2.20	6.630
550	-2.68	6.541
550	-3.39	6.431
550	-4.00	6.337
500	0	6.912
500	-0.17	6.901
500	-0.41	6.891
500	-0.67	6.879
500	-0.85	6.868
500	-1.35	6.837
500	-1.82	6.800
500	-2.42	6.728
500	-2.94	6.673
500	-3.39	6.584
500	-4.00	6.510
450	0	6.930
450	-0.17	6.922
450	-0.41	6.913
450	-0.67	6.911
450	-0.85	6.907
450	-1.35	6.897
450	-2.20	6.858
450	-4.10	6.711
400	0	6.930
400	-0.41	6.930
400	-0.85	6.929
400	-1.35	6.925
400	-2.20	6.901
400	-4.00	6.819
350	0	6.930
350	-0.41	6.930
350	-0.85	6.929
350	-1.90	6.930

Strobel, Solid St. Comm. 64, 513, 1987, Fig. 1

540	0	6.908
590	0	6.842
640	0	6.762
684.5	0	6.670
740	0	6.601
792	0	6.540
837	0	6.487
540	-0.62	6.841
590	-0.62	6.756
640	-0.62	6.650
684.5	-0.62	6.570
740	-0.62	6.499
792	-0.62	6.423
837	-0.62	6.352
540	-1.35	6.715
590	-1.35	6.597
640	-1.35	6.506
684.5	-1.35	6.420
740	-1.35	6.338
792	-1.35	6.273
837	-1.35	6.215
540	-1.98	6.592
590	-1.98	6.482
640	-1.98	6.389
684.5	-1.98	6.300
740	-1.98	6.232
792	-1.98	6.178
837	-1.98	6.141
540	-3.00	6.437
590	-3.00	6.320
640	-3.00	6.211
684.5	-3.00	6.148

Brynestad, Phys. Rev. B, Fig. 9

875	-2.13	6.0571
875	-1.90	6.0914
875	-1.69	6.1239
875	-1.46	6.1564
875	-1.24	6.1925
875	-1.01	6.2287
875	-0.79	6.2666
875	-0.57	6.3063
875	-0.36	6.3461
875	-0.14	6.3840
797	-2.13	6.1239
797	-1.90	6.1636
797	-1.69	6.2016
797	-1.46	6.2395
797	-1.24	6.2828
797	-1.01	6.3190
797	-0.79	6.3587
797	-0.57	6.3984
797	-0.36	6.4418
797	-0.14	6.4779
739	-2.13	6.1745
739	-1.90	6.2214
739	-1.69	6.2612
739	-1.46	6.3063
739	-1.24	6.3515
739	-1.01	6.3912
739	-0.79	6.4310
739	-0.57	6.4743
739	-0.36	6.5140
739	-0.14	6.5502
665	-2.13	6.2828
665	-1.90	6.3298
665	-1.69	6.3912
665	-1.46	6.4201
665	-1.24	6.4635
665	-1.01	6.5014
665	-0.79	6.5393
665	-0.57	6.5773
665	-0.36	6.6134
665	-0.14	6.6495
588	-2.13	6.4273
588	-1.90	6.4707
588	-1.69	6.5140
588	-1.46	6.5556
588	-1.24	6.5935
588	-1.01	6.6369
588	-0.79	6.6802
588	-0.57	6.7200
588	-0.36	6.7561
588	-0.14	6.7904
503	-2.13	6.6369
503	-1.90	6.6694
503	-1.69	6.7091
503	-1.46	6.7489
503	-1.24	6.7814
503	-1.01	6.8139
503	-0.79	6.8446
503	-0.57	6.8670
503	-0.36	6.8897
503	-0.14	6.9078

Yamaguchi, Japn. J. Appl. Phys. 27, L179, 1988, Fig.1

850	0	6.40
800	0	6.455
800	-0.699	6.335
800	-1.886	6.165
700	0	6.595
700	-0.699	6.473
700	-1.886	6.270
700	-2.658	6.170
600	0	6.760
600	-0.699	6.648
600	-1.886	6.438
600	-2.658	6.310
500	0	6.900
500	-0.699	6.840
500	-1.886	6.670
500	-2.658	6.535
400	0	6.970
400	-0.699	6.950
400	-1.886	6.888
400	-2.658	6.818
350	0	6.985
350	-0.699	6.972
350	-1.886	6.940
350	-2.658	6.890

Yamaguchi, Japn. J. Appl. Phys. 27 L179, 1988, Fig. 2

850	0	6.3763
800	0	6.4377
800	-1	6.2672
800	-2	6.1190
750	0	6.5102
750	-1	6.3317
750	-2	6.1721
700	0	6.5783
700	-1	6.3905
700	-2	6.2326
650	0	6.6533
650	-1	6.4812
650	-2	6.3113
650	-3	6.1872
600	0	6.7459
600	-1	6.5783
600	-2	6.3974
600	-3	6.2501
550	0	6.8282
550	-1	6.6727
550	-2	6.5045
550	-3	6.3543
500	0	6.8965
500	-1	6.8005
500	-2	6.6198
500	-3	6.4630
450	0	6.9425
450	-1	6.8825
450	-2	6.7656
450	-3	6.6019
400	0	6.9687
400	-1	6.9369
400	-2	6.8741
400	-3	6.7488
350	0	6.9845
350	-1	6.9680
350	-2	6.9354
350	-3	6.8682

Takayama-Muromachi, Japn. J. Appl. Phys. 26 L1156, 1987, Fig. 1

370	-0	7.00
413	-0.680	6.975
511	-0.680	6.87
593	-0.680	6.73
653	-0.680	6.61
697	-0.680	6.52
800	-0.680	6.37
900	-0.680	6.3
903	-0.680	6.27

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