Defect Structure of Nonstoichiometric Compounds – Verification Method

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ABSTRACT

This paper discusses the applicability of a thermodynamic approach to verify the models of defect structure of highly nonstoichiometric compounds. The proposed method is based on the mass action law and consists in analyzing the derivative of pressure dependence of defect concentration (or other parameter proportional to defect concentration) determined in a theoretical and an empirical way.

The analysis is carried out for selected systems with defect structures of different complexity, such as $Ti_{1+y}S_2$ $(Fe_{1-x}Mn)_{1-y}O$, $Na_xCo_{1+y}O_2$, $YBa_2Cu_3O_z$.

It is shown that the differences in pressure dependences of defect concentration and of electrical conductivity may be related to the intrinsic component of electrical conductivity, as in the case of $Ti_{1+y}S_2$ and $(Fe_{1-x}Mn)_{1-y}O$. the example of the solid solution $(Fe_{1-x}Mn)_{1-y}O$ indicates that increasing the concentration of defects leads to the formation of defect clusters, the types of which are proposed on the basis of proper analysis. The example of cobalt bronze, $Na_xCo_{1+y}O_2$, is presented in order to envisage the effect of nonstoichiometry in an alkali metal sublattice on electronic defects and consequently on defect concentrations in transition metal or oxidant sublattices. Different models of defect structure for this system are discussed. In the case of superconducting $YBa_2Cu_3O_z$, two alternative descriptions of defect structure are presented and a verification method is proposed.

1. INTRODUCTION

The development of crystallography at the beginning of the nineteenth century and the x-radiographic methods of the twentieth century, which provided useful tools for the determination of crystal lattices, nowadays appear insufficient for full description of nonstoichiometric crystals in which concentrations of point defects, such as vacancies, interstitials, electronic defects, depend on the temperature and activity of the gas phase being in equilibrium with the crystal. These defects are responsible for the transport properties of solids, i.e. diffusion and electrical properties. The theory of point defects in solids is a rational basis for the development of modern technologies and materials (electronics, ceramics), as well as for the understanding of high-temperature corrosion of metals and alloys and corrosion prevention. Miscellaneous uses of oxides, sulfides, carbides, nitrides or oxide bronzes having layered structures, ceramic superconductors or heterogeneous catalysts are closely related to imperfections and nonstoichiometry.

In this connection the problem arises how to determine the defect structure and defect concentration, especially for highly nonstoichiometric compounds in which the interactions of point defects give rise to defect complexes or clusters.

The present paper proposes how to verify different models of defect structure for highly nonstoichiometric

compounds. The verification method is based on proper interpretation of thermogravimetric measurements. The analysis is carried out for a number of oxide and sulfide systems with different defect structures, being a subject of the author's earlier investigations, such as $Ti_{1+y}S_2$, $(Fe_{1-x}Mn_x)_{1-y}O$, $Na_{0.7}Co_{1+y}O_2$ and $YBa_2Cu_3O_z$.

2. METHOD

In real crystals there exist two types of defects. These are crystallographic defects brought about by stresses accompanying crystal growth or external forces, and point defects which appear due to the fact that their presence lowers the free energy of crystals. These point defects are referred to as thermodynamically reversible and their concentration is dependent on the temperature and activity (pressure) of the gas atmosphere being in equilibrium with the crystal. The ionic defects (cation or anion vacancies, interstitials or defect aggregates, such as clusters or complexes) together with the electronic defects (quasi-free electrons and holes) are treated as individual species and defect formation is described by the following reaction:

$$\sum_i \nu_i A_i = 0 \qquad (1)$$

where A_i denotes reacting species, υ_i - stoichiometric coefficients (υ_i being positive for the products and negative for the substrates). The equilibrium constant is:

$$K = \exp(-\Delta G^{\circ}/RT) = \prod_i a_{A_i}^{\nu_i} \qquad (2)$$

where ΔG° denotes free enthalpy of defect formation, a_{Ai} - defect activity. Due to the fact that the majority of crystals are not highly defective, we can use defect concentrations instead of activities. In the case of non-stoichiometric compounds the equilibrium state depends on the activity (pressure) of gaseous species over the crystal, and therefore defect concentration is also influenced by this parameter.

Let us first consider a simple case of nickel oxide, $Ni_{1-y}O$, with doubly ionized cation vacancies as predominant defects. According to the Kröger Vink notation, the defect formation can be written as:

$$1/2O_2 = O_O + V''_{Ni} + 2h^{\cdot} \qquad (3)$$

and the corresponding equilibrium constant expressed in terms of molar fractions instead of activities is:

$$K = a_v a_h^2 / P_{O_2}^{1/2} \cong [V''_{Ni}][h^{\cdot}]^2 / P_{O_2}^{1/2} \qquad (4)$$

The crystal as a whole must be electrically neutral, so that

$$2[V''_{Ni}] = [h^{\cdot}] \qquad (5)$$

Finally we obtain the following equations describing the dependence of defect concentration on oxygen pressure.

$$[V''_{Ni}] = \sqrt[3]{K/2}\, P_{O_2}^{1/6} = \text{const}\, P_{O_2}^{1/6} = y = \text{const}\, P_{O_2}^{1/6} \qquad (6a)$$

$$[h^{\cdot}] = \sqrt[3]{2K}\, P_{O_2}^{1/6} \approx \sigma = \mu e [h^{\cdot}] = \text{const}\, P_{O_2}^{1/6} \qquad (6b)$$

As can be seen (Eq. 3), the variations of oxygen pressure bring about variations of defect concentration which are proportional to the observed weight changes of the crystal (specimen). Thus thermogravimetric measurements make it possible to find a real metal/oxidant ratio at given temperature and pressure conditions in equilibrium. Next, assuming a model of defect structure, we can find real deviation from stoichiometry (y) and the concentration of ionic defects. As follows from equation (6b), the function representing the dependence of concentration of holes, i.e. electronic defects, on oxygen pressure is of the same type. Therefore, by measuring electrical conductivity as a function of oxygen pressure we can check the correctness of the assumed model. Further on, we can calculate defect concentrations on the basis of known defect mobilities (μ).

In the above example we have found that cation vacancies, V''_{Ni} are predominant defects. It follows from the theory of point defects, however, that in pure crystals there may also be present singly ionized,

V'_{Ni}, or neutral, V^x_{Ni}, cation vacancies, with concentrations

$$[V'_{Ni}] = [h^{\cdot}] \sim \text{const } P_{O_2}^{1/4} \quad (6c)$$

$$[V^x_{Ni}] \approx \text{const } P_{O_2}^{1/2} \quad (6d)$$

if each of these defect types were the predominant one. The character of pressure dependence of ionic defect concentration (deviation from stoichiometry) and of electronic defect concentration (electrical conductivity) and especially the value of the exponent in the Eq. 6a, b, c, d are decisive for determination of the predominant defect types.

The assessment of defect structure requires taking into account all possible defect types, i.e. cation vacancies and interstitial cations as well as analogous defects in the anion sublattice. By determining respective equilibrium constants, it is possible to construct diagrams representing the relations between defect concentration and oxidant pressure /1-4/ which for each defect type are much more complicated than those given by Eq. 6.

The procedure described above has been successfully used for a very limited number of systems /1/, since the relations obtained in this way are mostly difficult to verify. The main reason is that thermogravimetric measurements are not sufficiently accurate and that the relations are expressed in terms of defect concentrations instead of activities. Consequently, in the majority of cases discussion is confined to the character of pressure dependence of the deviation from stoichiometry. In addition to thermogravimetric studies, variations of electrical conductivity or other properties proportional to defect concentration on oxidant pressure were analyzed. As the above mentioned relations between defect concentrations and oxidant pressure can be approximated by power functions, the experimental results are usually presented in a doubly logarithmic plot in order to analyze the derivative:

$$\partial \ln A / \partial \ln P_{O_2} = 1/n \quad (7)$$

If the value of this derivative remains constant within a certain pressure range, some hypotheses can be formulated regarding the type of predominant defects.

This introduction shows the procedure which is helpful in studying defect structure of nonstoichiometric compounds. The thermogravimetric measurements provide direct information on the type and concentration of ionic defects, whereas electrical conductivity measurements enable determination of types of electronic defects, provided the mobilities are independent of concentration. Additional information concerning the type of prevailing electronic defects (electrons or holes) is found from thermoelectric power measurements. Since in many systems the thermoelectric power is a function of electronic defect concentration, it is possible to find its dependence on oxidant pressure and to determine the value of the exponent, n, i.e. the type of point defects.

The presented experimental techniques provide complementary information. It should be noted that, due to very small variations of the measured quantities and a significant measuring error, reliable results can be obtained if the same sample is used or at least the samples are taken from the same series, if the measurements are performed in the same apparatus and under the identical temperature-pressure conditions. As follows from a comparison of experimental results from different laboratories, the discrepancies are generally so great that unequivocal interpretation is impossible. Therefore, the measurements of all the quantities dependent on oxidant pressure should be carried out simultaneously in the same experimental set-up.

3. COMPOUNDS WITH LOW DEFECT CONCENTRATIONS

As a matter of fact, the compounds with low defect concentrations are not the subject of this paper, but two of them, nickel and cobalt oxides, will be discussed in order to envisage the complexity of defect structure even in these relatively simple systems.

The nickelous oxide is a compound having relatively low defect concentration and its defect structure can be interpreted according to the procedure described in the previous section. The experimental results reported for $Ni_{1-y}O$ by other authors are inconsistent, regarding both deviation from stoichiometry itself (about 0.001 mole/mole) and its pressure dependence /2,3,5-11/. The value of the

exponent in Eq. 6, being approximately 1/5, indicates that singly and doubly ionized cation vacancies are present in comparable concentrations. This value of the exponent, as reported by many authors /7,.8,12/, may be related to impurities whose concentration easily reaches that of defects.

A similar situation is encountered in cobaltous oxide, $Co_{1-y}O$, in which defect concentration is higher by one order of magnitude, i.e. 0.01 mole/mole at 1000°C. The available results concerning deviations from stoichiometry and electrical conductivity are mostly quite consistent due to relatively high nonstoichiometry, but their interpretation is different /13-20/. Critical analysis of these results, carried out by Nowotny and Rekas /21/, has shown that the value of the exponent 1/n and its variation with oxygen pressure can be explained by the effect of donor- or acceptor-type impurities. They have shown further that good agreement between the experimental results and the theory is achieved if it is assumed that doubly ionized vacancies can interact, the interactions being taken into account by an activity coefficient determined from the Debye-Huckel theory. Finally they have demonstrated that for higher defect concentrations a satisfactory agreement is achieved with the assumption that defects are present in the form of clusters, $[(4V_{Co},Co_i]$, as suggested elsewhere /22-4/. This analysis indicates that even for a system as simple as cobaltous oxide it becomes difficult to decide what the real defect structure is like and what the concentrations of different defect types are. A similar situation is observed for almost every simple oxide having semiconducting properties. The formation of ionic defects gives rise to an equivalent number of electronic defects. This means that in the band gap additional acceptor or donor levels appear, and charge transport depends on the concentration of electronic defects. Correct interpretation of thermogravimetric measurements can be given after careful analysis of different models of defect structure with and without interactions of ionic defects. The electronic structure should also be analyzed and the results of both should be taken into account.

4. COMPOUNDS WITH INTRINSIC CONDUCTIVITY ($Ti_{1+y}S_2$)

High nonstoichiometry is always associated with defect interactions resulting, on the one hand, from a higher concentration of defects and, on the other hand, from interatomic forces brought about by varying metal-metal distances. This may lead to the formation of an acceptor or donor band. Crystals with high deviations from stoichiometry exhibit generally a quite narrow energy gap (0.5-1.5 eV) due to which already at moderate temperatures electrons from the valence band can easily get to the conduct band. In such a case the electrical conductivity consists of at least two components, one related to nonstoichiometry, σ_y and the other being the intrinsic conductivity σ_o:

$$\sigma = \sigma_o + \sigma_y = \sigma_o + AP_{O_2}^{-1/n} \sim \text{const } P_{O_2}^{-1/n} \qquad (8)$$

The exponents in equations describing pressure dependence of the deviation from stoichiometry and electrical conductivity will be different. Such a situation is observed for titanium disulfide which is defective in the cation sublattice, titanium ions in interstitial positions being the predominant ionic defects in $Ti_{1+x}S_2$. Its deviation from stoichiometry falls in the range 0-0.15 mole/mole /25,26/. The reaction of defect formation can be written as follows:

$$TiS_2 = Ti_i^{z+} + S_2 + ze' \qquad (9)$$

and the dependence of ionic defect concentration on sulfur pressure:

$$y = [Ti_i^{z+}] = \text{const } P_{S_2}^{-1/(z+1)} \qquad (10)$$

where z assumes values from 1 to 4.

It can be stated on the basis of the results reported by Saeki /25/ and Winn, Steele /26/ that the relation between the deviation from stoichiometry and sulfur pressure can be described as follows:

$$y = \text{const } P_{S_2}^{-1/n} \qquad (11)$$

with the exponent close to -1/2.5 /27/, which means that interstitial titanium ions at 1+ and 2+ ionization degree should be the dominating defects (Eq. 10). Thus, in titanium disulfide, electrons and titanium interstitials interact due to which the effective ionization degree of the ionic defects decreases.

Thermoelectric power measurements have supported the conclusion drawn on the basis of thermogravimetric studies. The negative sign of thermoelectric power in wide temperature and sulfur pressure ranges proves that the dominating charge carriers are electrons formed due to ionization of the interstitial titanium atoms acting as donor centers /27-31/.

Electrical conductivity measurements have revealed that in the range of small deviations from stoichiometry the relation between electrical conductivity and sulfur pressure is described by an equation similar to Eq. 8, with the exponent being -1/3.5 /27/. However, the analysis has shown that the electrical conductivity is a sum of two components: σ_o being independent of nonstoichiometry and σ_y being dependent on y. The activated character of the σ_o component (Fig. 1) indicates that this component is associated with the generation of charge carriers through the energy gap. The energy gap estimated on the basis of these measurements equals 0.8 eV and remains in good agreement with optical measurements /28/. It has also been shown that the conductivity component, σ_y, is

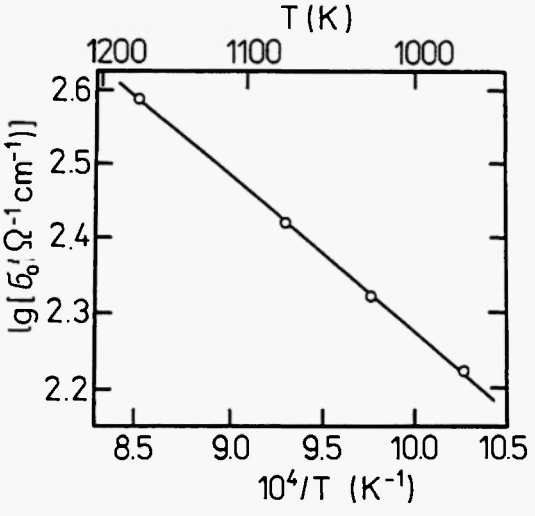

Fig. 1: Dependence of σ_0-component of electrical conductivity of $Ti_{1+y}S_2$ on temperature.

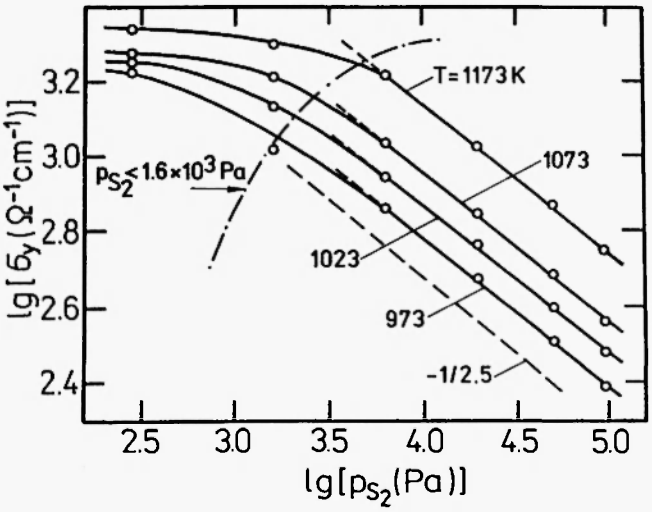

Fig. 2: Dependence of σ_y-component of electrical conductivity of $Ti_{1+y}S_2$ on sulphur pressure at different temperatures.

closely related to the deviation from stoichiometry and that its dependence on sulfur pressure in the range 10^3-10^5 Pa is analogous to that of the deviation from stoichiometry, the exponent being 1/2.5 (Fig. 2). At lower sulfur pressures, i.e. at high defect concentrations, the relation between electrical conductivity and sulfur pressure becomes more complex. The properties of titanium disulfide have been discussed in detail in one of the earlier papers /27/. To sum up, in titanium disulfide, for which deviations from stoichiometry change in the range 0.01-0.1 mole/mole at temperatures 973-1173K, the dominating defects are interstitial titanium ions with ionization degrees +1 and +2. Lowering of the effective ionization degree is associated with interactions between the ionic defects and quasi-free electrons. Electrical properties are a joint effect of thermally activated electrons (intrinsic carriers) and electrons related to the deviation from stoichiometry (donor band).

5. CRYSTALS WITH DEFECT CLUSTERS $(Fe_{1-x}Mn_x)_{1-y}O$

As the deviation from stoichiometry increases, the defect structure becomes more complex. For illustration, the deviation from stoichiometry of ferrous

oxide, being in the range 0.05-0.17 mole/mole, is related to cation vacancies /32,35/. The cation vacancies interact with interstitial iron ions resulting from Frenkel disorder and form defect clusters. The existence of defect clusters has been evidenced by X-ray neutron diffraction /36-41/, high resolution electron microscopy /42-44/ and theoretical calculations /22,45-47/. The electronic defects, i.e. holes, form an acceptor band, the properties of which are modified by increasing deviation from stoichiometry. In order to envisage the modification of defect structure, the author and coworkers /48-50/ studied the deviation from stoichiometry together with the electrical conductivity and thermoelectric power of ferrous oxide doped with manganese. Doping with manganese lowered the deviation from stoichiometry and modified the electrical properties toward the semiconducting ones. The equations describing pressure dependences of the deviation from stoichiometry:

$$y = \text{const}\ P_{O_2}^{1/n_y} \qquad (12a)$$

and electrical conductivity:

$$\sigma = \text{const}\ P_{O_2}^{1/n_\sigma} \qquad (12b)$$

had different values of exponents, n_y and n_σ, which is illustrated in Table 1. As in the case of ferrous oxide /51/ and titanium disulfide, it has been assumed that this system exhibits some intrinsic conductivity and, consequently, its electrical conductivity is a sum of two components, the intrinsic one and that related to the deviation from stoichiometry. This permitted separation of both components. The activated nature of the thus found intrinsic conductivity has made it possible to estimate the energy gap which appeared consistent with optical measurements within the limits of measuring error. Fig. 3 presents the dependence of intrinsic conductivity, σ_0, on temperature in the Arrhenius plot and Table 2 gives the values of energy gap calculated

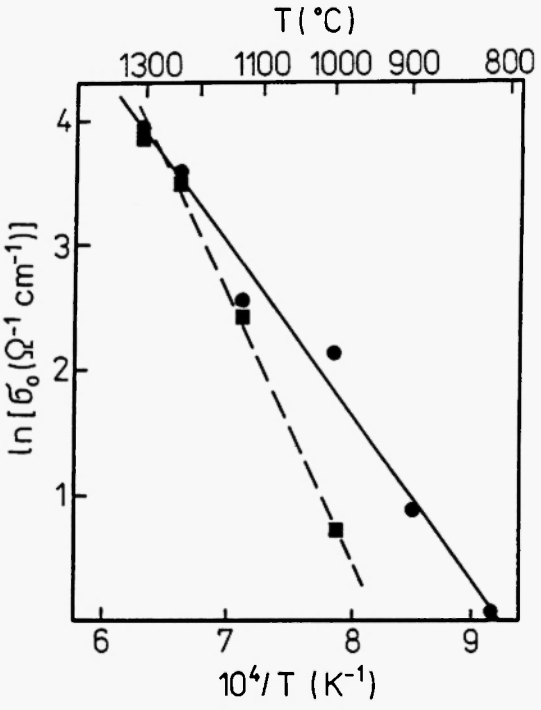

Fig. 3: Dependence of σ_0-component of electrical conductivity on temperature of $Fe_{1-y}O$ (•) and $Fe_{0.878}Mn_{0.122}O$ (■)

Table 1
The empirical parameters A_i and E_g of $(Fe_{1-x}Mn_x)_{1-y}O$ /50/

	A_i ($\Omega^{-1}cm^{-1}$)	E_g (eV)
x_{Mn} = 0.000	2.4×10^5	2.4
0.037	6.1×10^6	3.06
0.122	1.3×10^7	3.38
1.000		3.2 (ref./53/)

$\sigma_o = A_i \exp(-E_g/2kT)$

Table 2
Empirical and theoretical exponents in equations describing the dependence of nonstoichiometry and electrical conductivity of $(Fe_{1-x}Mn_x)_{1-y}O$ /49/

T (K)	y range (mol/mol)	$n_y^{\bullet}$ (exper)	$n_y^{\bullet}$ (Eq. 15)	(m:n)$^{-}$	$n_\sigma^{\bullet\bullet}$	$n_{\sigma_y}^{\bullet\bullet\bullet}$
		x=0.037				
1273	0.040-0.074	3.4±0.06	3.0-3.5	$(4:1)^{3-}$	4.1	3.6
			3.1-3.7	$(16:5)^{14-}$		
			3.2-3.7	$(12:4)^{10-}$		
			2.9-3.4	$(6:2)^{4-}$		
			3.3-3.9	$(8:3)^{6-}$		
			3.1-3.8	$(10:4)^{7-}$		
	0.074-0.101	7.1±0.2	5.8-6.8	$(2:1)^{2-}$	7.3	7.2
1403	0.037-0.075	2.6±0.1	2.2-2.6	$(4:1)^{2-}$	3.8	2.5
			2.5-2.9	$(16:5)^{11-}$		
			2.3-2.7	$(6:2)^{3-}$		
			2.3-2.8	$(8:3)^{4-}$		
			2.3-2.8	$(10:4)^{5-}$		
	0.075-0.102	8.4±0.3	5.9-6.9	$(2:1)^{2-}$	10.1	8.0
1473	0.036-0.77	2.2±0.1	2.2-2.6	$(4:1)^{2-}$	4.2	2.2
			1.7-2.1	$(6:2)^{2-}$		
			1.9-2.3	$(8:3)^{3-}$		
	0.077-0.116	4.6±0.3	5.9-7.5	$(2:1)^{1-}$	6.3	4.2
		x=0.122				
1273	0.029-0.052	3.2±0.1	2.9-3.2	$(4:1)^{3-}$	3.7	3.3
			3.0-3.3	$(16:5)^{14-}$		
			3.0-3.4	$(12:4)^{10-}$		
			2.7-3.1	$(6:2)^{4-}$		
			3.1-3.5	$(8:3)^{6-}$		
			3.0-3.3	$(10:4)^{7-}$		
	0.052-0.072	5.9±0.1	5.2-5.9	$(2:1)^{2-}$	6.1	5.7
1403	0.023-0.047	2.8±0.1	2.9-3.2	$(4:1)^{3-}$	3.8	2.7
			2.6-2.9	$(16:5)^{12-}$		
			2.6-3.1	$(12:4)^{9-}$		
			2.7-3.0	$(6:2)^{4-}$		
			2.6-3.0	$(8:3)^{5-}$		
			2.6-3.0	$(10:4)^{6-}$		
	0.047-0.081	6.0±0.2	5.1-6.1	$(2:1)^{2-}$	6.6	5.6
1473	0.023-0.049	2.3±0.1	2.2-2.4	$(4:1)^{3-}$	4.1	2.3
			2.2-2.5	$(10:4)^{5-}$		
			2.2-2.5	$(8:3)^{4-}$		
	0.049-0.083	5.3±0.3	5.1-6.1	$(2:1)^{1-}$	7.4	5.2

(•) $y=\text{cont}P_{O_2}^{1/n_y}$ (••) $\sigma=\text{cont}P_{O_2}^{1/n_\sigma}$, (•••) $\sigma_y=\text{cont}P_{O_2}^{1/n_{\sigma_y}}\sigma_y$

from the electrical conductivity measurements and determined by optical methods for pure oxides /52,53/.

The pressure dependence of the other component of electrical conductivity, σ_y, related to nonstoichiometry, is consisted with that of the deviation from stoichiometry (exponent $1/n_y$) which is shown in Table 1. The values of the exponents, 1/n, together with their variation with oxygen pressure and temperature indicate, however, that the defect structure of this crystal is rather complex.

The defect structure was analyzed according to the method proposed by Kofstad and Hed /54/ and further

developed by Rekas and Mrowec /55/. The method involves determination of the equilibrium constant of cluster formation. It has been assumed that in mangano-wustite the defects form an ideal solution and that one type of defect clusters dominates in each non-stoichiometry range. The tests were carried out for the cluster models postulated in the literature for undoped ferrous oxide, i.e. 2:1, 4:1, 6:2, 8:3, 10:4, 12:4, 16:5 (ratio of cation vacancies and interstitial ions m:n = $[mV_{Me},nMe_i]$). Thus the experimental values $\partial \ln y / \partial \ln P_{O_2}$ were compared with the theoretical ones, calculated for different cluster models with different ionization degrees. Next the dependence of the equilibrium constant of defect or cluster formation on nonstoichiometry was analyzed in order to find out which type of cluster would be suitable to fit the experimental results.

The following equations were used to calculate the equilibrium constants of defect formation for clusters with ionization degree J, consisting of m cation vacancies and n interstitial ions $(mV_{Fe}:nFe_i)^{J-}$:

$$(n+J)Fe_{Fe} + nV_t + (m-n)/2O_2 = [(V_{Fe})_m (Fe_i^{\cdot\cdot\cdot})_n]^{J-} + (m-n)O_O + JFe_{Fe}^{\cdot} \quad (13)$$

where: $O<J<(2m-3n)$, V_t is an interstitial tetrahedral site available to the complex defect,

$$K_J = \frac{y^{J+1} a_J}{[m-n-(J+m)y]^{n+J} (2-ay/(m-n))} P_{O_2}^{-(m-n)/2} \quad (14)$$

where $a_J = J^J(m-n)^{n-1}$ for $J \neq 0$ and $a_J = (m-n)^{n-1}$ for $J=0$ and "a" denotes the number of tetrahedral sites neighbouring upon the cation vacancies that belong to the cluster under consideration /55/. Theoretical values of the differential $\left(\partial \ln P_{O_2} / \partial \ln y\right)$ were calculated by differentiation of Eq. (14). The following expression has been obtained:

$$n_y = (\partial \ln P_{O_2} / \partial \ln y) = \frac{2}{m-n} \frac{(n+J)(m+J)y}{n-m-(J+m)y} + \frac{ay}{2(m-n)-ay} + J+1 \quad (15)$$

In order to verify the type of dominating defect clusters in $(Fe_{1-x}Mn_x)_{1-y}O$, the values of the exponent, n_y, for different clusters were calculated (Eqs. 15 and 13) and compared with the experimental ones. Table 1 shows the examples of such a comparison together with the suggested type of prevailing defect clusters, the detailed discussion having been published elsewhere /48/.

It can be concluded that for the low Mn-doped ferrous oxide there exist two ranges of the deviation from stoichiometry, y, in which two different types of defect clusters may dominate. More than one type of defect clusters may be fit at low nonstoichiometry. In the range of higher deviations from stoichiometry, the best fit for all the investigated temperatures has been obtained for singly ionized Roth's clusters. The results obtained in this study are consistent with those reported in the literature /37-40/ as regards the types of proposed predominant defect clusters. In addition, pressure ranges in which each type of defect cluster may be the dominating one are given.

The procedure described above for analysis of the results of thermogravimetric measurements is based on the mass action law with the assumption that the activities of defect clusters are approximately equal to their concentrations. Such an assumption is too simplified at high defect concentrations and, therefore, it is rather difficult to decide which type of defect clusters is actually the predominant one. The analysis of thermogravimetric measurements in conjunction with electrical properties of a nonstoichiometric compound, pure and doped with an element slightly modifying its defect structure, has proved the existence of defect clusters and has limited the number of possible cluster types. It seems that this method is suitable for numerical calculations and it might be helpful in analyzing crystal structures.

6. VERIFICATION OF DEFECT TYPES IN COMPLEX COMPOUNDS

6.1. Na_xCoO_2

The examples of simple oxides and sulfides described in the previous sections illustrate the situation where defect structure becomes complex due to interactions. A much more complicated situation is encountered when defects can be present in more than one sublattice as in spinel-type compounds, perovskites

or oxide bronzes. This problem was first approached by the author and coworkers /56/ while analyzing the defect structure of $Na_{0.7}CoO_2$. This compound has a layered structure, the layers being built of CoO_6 octahedra. Sodium ions occupy the positions between the CoO_2 layers and their concentration can vary in a quite wide range /57/. The results of thermogravimetric and electrical conductivity measurements /56,58/ at different oxygen pressures (Figs. 4 and 5) indicate non-stoichiometry in the oxygen-cobalt sublattice, the following relations having been found:

$$y = \text{const } P_{O_2}^{-1/n_y} \quad (16a)$$

$$\sigma = \text{const } P_{O_2}^{1/n_\sigma} \quad (16b)$$

The values of exponents in different temperature and oxygen pressure ranges are given in Table 3. As can be seen, the derivative of the function representing the dependence of nonstoichiometry on oxygen pressure is negative and its absolute value falls in the range 0.98-0.65, whereas the analogous derivative of electrical conductivity is positive and assumes a small value of 0.05. In contrast to the examples presented earlier, the concentration of electronic defects is not proportional to that of ionic defects and its dependence on oxygen pressure is different. Many authors assume the notation Na_xCoO_{2-y} to describe the character of deviation from stoichiometry in this compound. This notation is in agreement with the observed weight loss of the oxide with decreasing oxygen pressure and suggests the occurrence of oxygen vacancies, formed in the reaction:

$$O_O^x = 1/2O_2 + V_O^{\cdot\cdot} + 2e' \quad (17)$$

It follows from this equation that the formation of oxygen vacancies should be accompanied by quasi-free electrons, the concentration of which should increase with decreasing oxygen pressure and the value of the exponent should be similar to that for the deviation from stoichiometry. This, however, has not been actually observed. The positive sign of thermoelectric power together with the character of pressure dependence of electrical conductivity indicate that electron holes are the dominating electronic defects. Their existence may be accounted for by vacancy

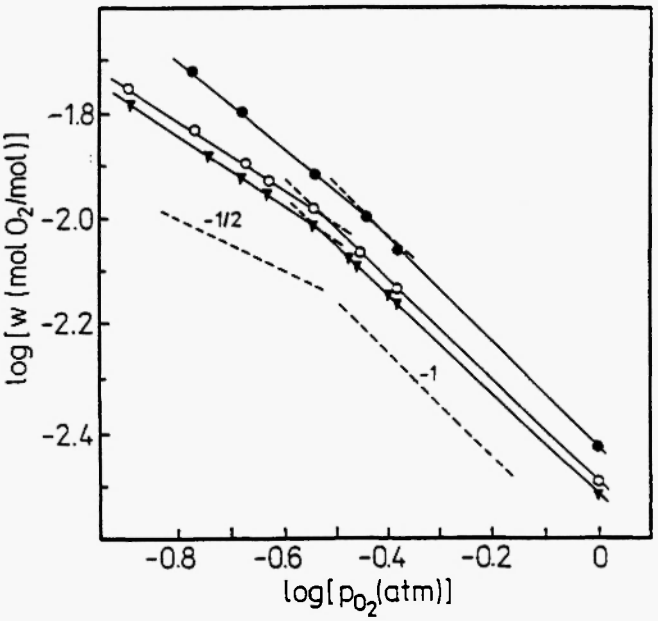

Fig. 4: Dependence of deviation from stoichiometry in $Na_{0.7}CoO_2$ on the oxygen pressure for temperatures: (•) 990 K, (O) 935 K, (▲) 905 K.

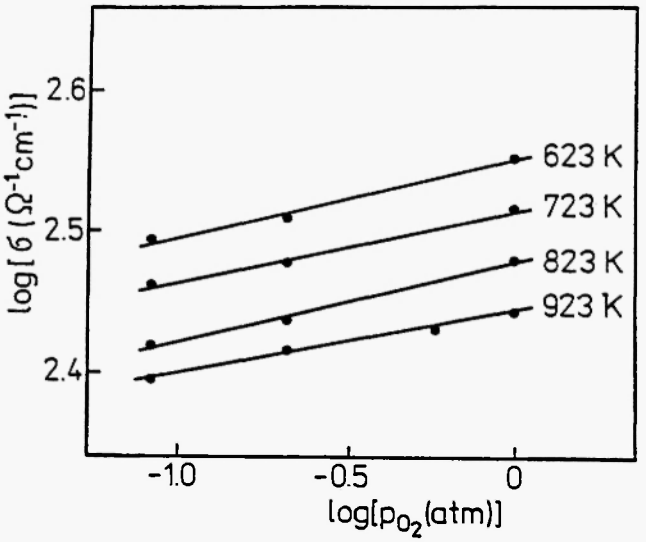

Fig. 5: Dependence of electrical conductivity in $Na_{0.7}CoO_2$ on the oxygen pressure for several temperatures.

formation in the sodium sublattice, $V_{Na}^{\cdot}$, and a simultaneous change in the ionization degree of cobalt from 3+ to 4+. Appearance of Co^{+4} ions is equivalent to the

Table 3
The exponents of the dependences of the deviation from stoichiometry and electrical conductivity on oxygen pressure (Eqs. 16a and 16b).

T (K)	Range P_{O_2} (atm)	$-1/n_w$	$1/n_h$
990	1 - 0.36	0.98	
	0.36-0.17	0.82	
935	1 - 0.29	0.96	
	0.29-0.13	0.65	
923	1 - 0.10		0.045
905	1 - 0.29	0.96	
	0.29-0.13	0.67	
823	1 - 0.10		0.055
723	1 - 0.10		0.050
623	1 - 0.10		0.056
	error	Δ=±0.02	Δ=±0.008

appearance of (1-x) moles of electron holes. The reaction of defect formation should then be written as follows:

$$O_O^x + 2h^{\cdot} = V_O^{\cdot\cdot} + 1/2O_2 \qquad (18a)$$

or

$$O_O^x + h^{\cdot} = V_O^{\cdot} + 1/2O_2 \qquad (18b)$$

if singly ionized vacancies dominate.

As the concentration of sodium vacancies is quite big and diffusion of ions in this sublattice is faster than in the oxygen sublattice, it seems purposeful to consider also such defects as cobalt ions in sodium sites which may be formed in the reaction:

$$Co_{Co}^x + 2O_O^x + 2V'_{Na} + 4h^{\cdot} = Co_{Na}^{\cdot\cdot} + O_2 \qquad (19)$$

It follows from this equation that decreasing the oxygen pressure would favor the formation of such ionic defects (weight loss would be observed in thermogravimetric measurements), and at the same time it would lower the concentration of electronic defects (electrical conductivity), which is in agreement with the experimental results.

In order to determine the predominant type of defects occurring in the cobalt bronze Na_xCoO_2, it is necessary to find the pressure dependences of ionic and electronic defect concentrations according to Eqs. (18) and (19) and compare them with the experimental results. The dependence of defect concentration on oxygen pressure can be determined on the basis of an equilibrium constant for the reaction of defect formation and an electroneutrality condition which for the reactions (18a) and (19) can be written as follows:

$$K_{18} = a_{V_O} P_{O_2}^{1/2} / a_h^2 \qquad (20)$$

$$[V'_{Na}] = 2[V_O^{\cdot\cdot}] + [h^{\cdot}] \qquad (20a)$$

and

$$K_{19} = a_{Co_{Na}} P_{O_2} / a_h^4 a_{V_{Na}}^2 \qquad (21)$$

$$[V'_{Na}] = [h^{\cdot}] + 2[Co_{Na}^{\cdot\cdot}] \qquad (21a)$$

where a denotes defect activity, [ ] - defect concentration in moles/mole of the compound. With the assumption that defect activity is approximately equal to its concentration, the dependences of oxygen vacancy and

electron hole concentration on oxygen pressure are:

$$K_{18}(1-x-2y)^2 = y\, P_{O_2}^{1/2} \quad (22)$$

$$K_{18}[h^{\cdot}]^2 = \frac{1}{2}(1-x-[h^{\cdot}])\, P_{O_2}^{1/2} \quad (23)$$

where

$$[V_O^{\cdot\cdot}] = y, \quad [V'_{Na}] = 1-x, \quad [h^{\cdot}] = 1-x-2y$$

and similarly for cobalt ions:

$$K_{19}(1-x-2y)(1-x-4z)^{\cdot} = z\, P_{O_2} \quad (24)$$

$$K_{19}[h^{\cdot}]^4\{1-x-\tfrac{1}{2}(1-x-[h^{\cdot}])\}^2 = \tfrac{1}{4}(1-x-[h^{\cdot}])P_{O_2} \quad (25)$$

where $\left[Co_{Na}^{\cdot\cdot}\right] = z$, $\left[V'_{Na}\right] = 1-x-2z$, $[h'] = 11-x=4z$.

The complexity of these relations disables direct assessment of the pressure dependence of defect concentration. Nevertheless, it helps in determining the dependence between the derivative $d\ln[def]/d\ln P_{O_2}$ and ionic defect concentration. The derivatives were calculated by differentiation of the obtained implicit functions. For oxygen vacancies the following relations have been found:

$$d\ln y/d\ln P_{O_2} = -\frac{1}{2}(1-x-2y)/(1-x+2y) = \quad (26)$$
$$= -\frac{1}{2}(1-x-2w)/(1-x+2w) = n_w^{-1}$$

$$d\ln[h^{\cdot}]/d\ln P_{O_2} = \quad (27)$$
$$y/(1-x+2y) = w/(1-x+2w) = n_h^{-1}$$

whereas for cobalt ions $Co_{Na}^{\cdot\cdot}$

$$\frac{d\ln z}{d\ln P_{O_2}} = -\left(\frac{4z}{1-x-2z} + \frac{16z}{1-x-4z} + 1\right)^{-1} = \quad (28)$$
$$-\left(\frac{2w}{1-x-w} + \frac{8w}{1-x-2w} + 1\right)^{-1} = n_w^{-1}$$

$$\frac{d\ln[h^{\cdot}]}{d\ln P_{O_2}} = \left(\frac{1-x-4z}{1-x-2z} + \frac{1-x}{4z} + 3\right)^{-1} = \quad (29)$$
$$\left(\frac{1-x-2w}{1-x-w} + \frac{1-x}{2w} + 3\right)^{-1} = n_h^{-1}$$

As follows from the above calculations, the obtained derivatives, being equivalent to the exponents in Eqs.(16a) and (16b), are dependent on defect concentration at constant x. The defect concentrations y and z are closely related to the w-quantity referred to as the deviation from stoichiometry expressed in moles/mole of $Na_{0.7}CoO_2$. As follows from Eqs. (18) and (19) y = w and z = 1/2w. Eqs. 26-28 can thus be expressed as functions of w.

Fig. 6 shows the functions described by Eqs. (26) and (28) for x=0.3 together with the analogous functions for the defects with different ionization degree $\left(V_O^{\cdot}, Co_{Na}^{\cdot}, Co_{Na}^{\cdot\cdot}\right)$ obtained as described above. Fig. 7 shows, in turn, the functions given by Eqs. (27)

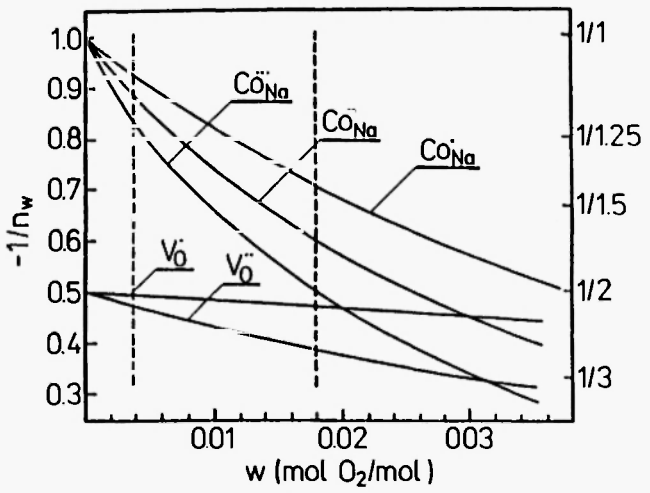

Fig. 6: Dependence of the exponent $1/n_w$ (Eqs. 26 and 28) as a function of nonstoichiometry for defects of different ionization degree.

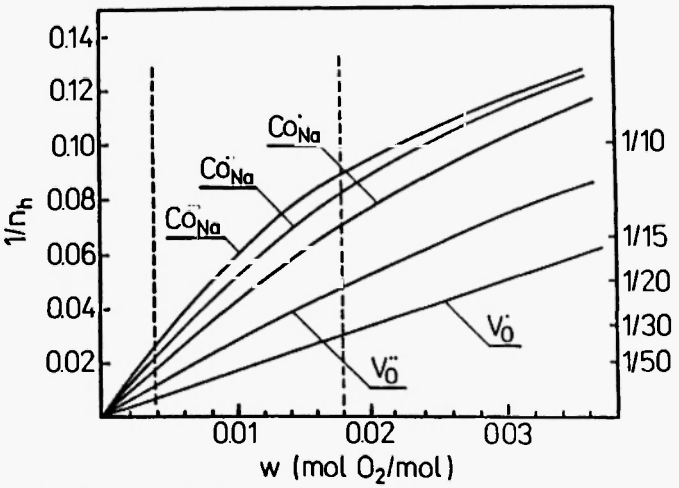

Fig. 7: Dependence of the exponent $1/n_h$ (Eqs. 27 and 29) as a function of nonstoichiometry for defects of different ionization degree.

and (29) as well as the analogous functions for the defects with different ionization degree. From the theoretical calculations presented in Fig. 7 it follows that the $d\ln[h^{\cdot}]/d\ln P_{O_2}$ derivative, for both types of defects, has relatively small positive values, which is consistent with the experimentally obtained value of the exponent in Eq. (16b). For the ionic defects the discussed dependences are different. The values of derivatives are negative. The values of exponents listed in Table 3 indicate that the predominant ionic defects in the cobalt bronze, except for sodium vacancies, are cobalt ions Co^{3+} substituted for sodium. It should be noted that the above calculations have been carried out with the assumption that the activity of defects is equal to their concentration, which at the concentration 0.3 moles/mole cannot be fully justified. The relatively small values of the exponent in the dependence of electrical conductivity on oxygen pressure, as well as the insufficient accuracy of its determination, make it impossible to decide unequivocally which type of defects is the predominant one on the basis of insignificant differences between the corresponding $1/n_h$ exponents. On the contrary, the differences observed in the derivative for the function $\ln[def] = f(\ln P_{O_2})$ for oxygen vacancies and cobalt ions are sufficiently big. The X-ray and EPR analyses of the samples have shown the existence of defects within the cobalt sublattice, but big experimental errors disable any conclusions concerning the defect types. Therefore, the analysis proposed in this work remains the only method for determining the type of predominant defects.

6.2. $YBa_2Cu_3O_z$

Another interesting problem arises in analyzing the defect structure of a superconducting compound $YBa_2Cu_3O_z$. this compound is known in two polymorphous forms, an orthorhombic and a tetragonal one, schematically shown in Fig. 8. The low-temperature orthorhombic form (stable up to 800-1000K, depending on oxygen pressure) can be described by a formula $YBa_2Cu_3O_{7-y}$, oxygen vacancies being formed due to oxygen departure from the 0(1) lattice sites. The tetragonal form does not differ from

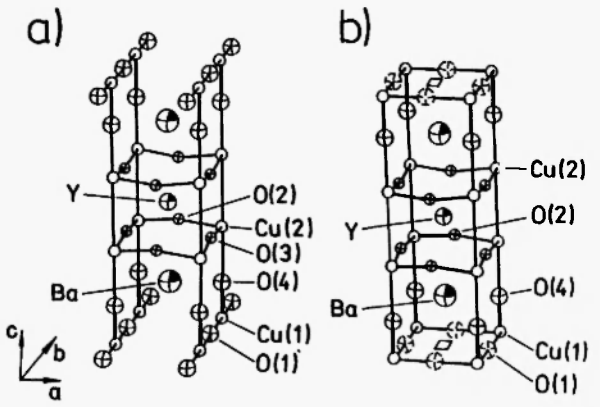

Fig. 8: Structure of $YBa_2Cu_3O_z$, a) the orthorhombic, b) the tetragonal phase.

the orthorhombic one in the arrangement of atoms but in parameters a and b which become equal. Further increase of nonstoichiometry consists in oxygen loss, all the 0(1) sites being available to oxygen atoms. At the highest investigated temperature, 1200K, and at an oxygen pressure below 10^2Pa, the chemical composition of this oxide approaches $YBa_2Cu_3O_6$. If oxygen vacancies were the predominant ionic defects in this compound, as commonly accepted in the literature, the defect formation would be written as follows:

$$O_O = 1/2O_2 + V_O^{\cdot\cdot} + 2e' \qquad (30)$$

which, however, does not find confirmation in electrical properties. It has been found, namely, that within its stability range the orthorhombic phase exhibits metal-type conductivity with electron holes as dominating charge carriers. If oxygen vacancies and holes are accepted as dominating defects, the negatively charged species, the presence of which would satisfy the electroneutrality condition, are lacking. On analyzing the crystal structure of this compound, the author and coworkers /55/ have postulated the existence of some lattice sites which might be easily occupied by cations and might play a role of cation vacancies. The electroneutrality condition would then be:

$$[h^{\cdot}] + 2[V_O^{\cdot\cdot}] = [V_M'] \qquad (31)$$

The existence of cation vacancies in the discussed system appears to be a reasonable assumption. Voids in the Cu(2)-0(2) or Cu(1)-0(1) planes (Fig. 8) can be

occupied by the M^{1+} cations. In order to demonstrate that the introduction of metal ions into the structure of this oxide can actually take place, an electrochemical intercalation of such metal ions as Cu, Na and Li was carried out at room temperature in the cell Me/ $Me^{+}/Me_xYBa_2Cu_3O_{7-y}$. The authors have succeeded in introducing about 0.6 mole/mole of copper ions, about 0.35 mole/mole of sodium ions and about 1.6 mole/mole lithium ions /59,60/. It has been shown that intercalation by heating at a high temperature is also possible. Chemical analysis confirmed the amount of metal ions introduced into the oxide. As shown earlier /59,60/, the alkali metals significantly influence the conductivity of $YBa_2Cu_3O_7$, but only slightly shift the T_C point of superconductivity. The same result has been obtained by other authors /61-65/ The above investigations prove that voids existing in the crystal structure of $YBa_2Cu_3O_7$ can be occupied by metal ions and thus can be treated as cation vacancies, V_M.

The existence of electron holes in the amount of up to 1 mole/mole of the compound with a "stoichiometric" composition (y=0) is not consistent with the experimental results, as already mentioned. The concentration of electron holes at low temperatures is estimated at 0.1-0.2 mole/mole and at higher temperatures - at 0.4-0.6 mole/mole /66-68/. These lower concentrations of electron holes may result from their interactions with singly ionized cation vacancies to produce electroneutral cation vacancies:

$$V'_M + h^{\cdot} = V^x_M$$

According to Eq. 30 any oxygen atom escaping from the crystal lattice leaves behind two electrons. These electrons might change the ionization degree of the copper ions $Cu^{2+}(2)+e'=Cu^{1+}(2)$. In such a case there would exist two independent types of electronic defects, i.e. holes and electrons. With increasing deviation from stoichiometry one should expect an increase in the electrical conductivity, whereas a quite opposite effect is actually observed /68-71/. For this reason it appears more likely that electrons react with holes (compensation effect) and the reaction of defect formation can be expressed as:

$$2h^{\cdot} + O_O = 1/2O_2 + V^{\cdot\cdot}_O \qquad (32)$$

If it is assumed, in agreement with the previous considerations, that the maximum concentration of electron holes at a given temperature, when y=0, equals a_h, then according to the above model, their concentration will change in the following way:

$$[h^{\cdot}] = a_h = 2y$$

Thus, the complete compensation of holes should take place at $y=a_h/2$. Consequently, if it is assumed that the concentration of electron holes in a stoichiometric compound is 0.4-0.6 mole/mole, then compensation should be observed at a deviation from stoichiometry of 0.2-0.3 mole/mole which, however, is smaller than the deviation at which the o-t phase transition actually takes place.

As follows from the above model, at higher deviations from stoichiometry there should appear singly ionized oxygen vacancies, i.e. defect complexes made up of doubly ionized oxygen vacancies and electrons ($V^{\cdot}_O$,e'), which appear due to interactions between the V_O vacancies and the $Cu^{1+}(1)$ ions in the reaction:

$$h^{\cdot} + O_O = 1/2O_2 + V^{\cdot}_O \qquad (33)$$

This model of defect structure is qualitatively consistent with the variations of the deviation from stoichiometry, which increases with decreasing oxygen pressure, and the variations of electrical conductivity, which in turn decreases with decreasing oxygen pressure (negative value of the derivative $d\ln y/d\ln P_{O_2}$ Fig. 9 and a positive value of the derivative for the dependence of electrical conductivity on oxygen pressure /69-73/.

In the above model the concept of free-electron formation without any change in the concentration of electron holes has been rejected. It cannot be excluded, however, that singly ionized oxygen vacancies dissociate, bringing about the formation of free electrons and a drop in the concentration of electron holes. this reaction could be written as follows:

$$h^{\cdot} + O_O = 1/2O_2 + V^{\cdot\cdot}_O + e' \qquad (34)$$

The reactions of defect formation in the above model do not involve changes in charge carriers concentration. As the mobilities of electrons and holes are unknown, it

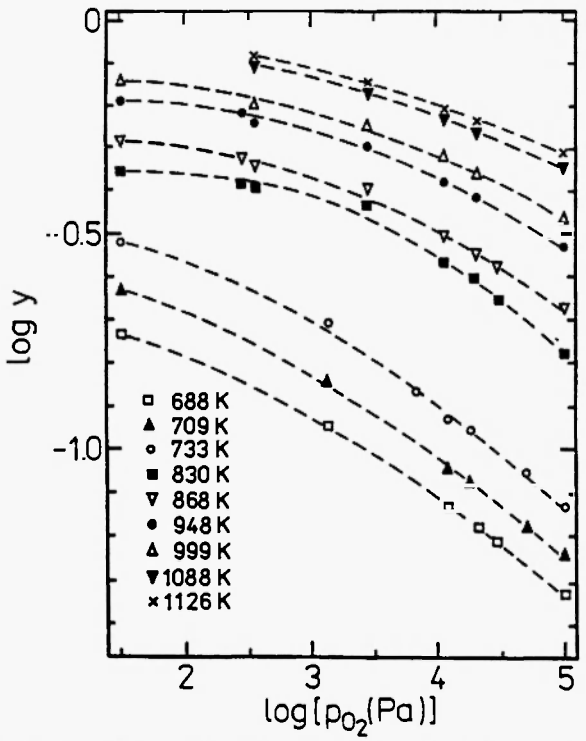

Fig. 9: The dependence of deviation from stoichiometry in $YBa_2Cu_3O_{7-y}$ on equilibrium oxygen pressure at different temperatures.

is difficult to predict the character of pressure dependence of electrical conductivity.

In the opinion of many authors /68,72-74/, $YBa_2Cu_3O_z$ can be described by the formula $YBa_2Cu_3O_{6+x}$, which means that its deviation from stoichiometry results from the formation of "interstitial" oxygen ions occupying the 0(1) sites. The reactions of defect formation can be written as follows:

$$1/2O_2 + V_i = O_i'' + 2h^{\cdot} \quad (35)$$

$$1/2O_2 + V_i = O_i' + h^{\cdot} \quad (36)$$

$$1/2O_2 + V_i = O_i^x \quad (37)$$

where O_i'', O_i' and O_i^x denote doubly and singly ionized and neutral oxygen atoms, respectively, in "interstitial" positions, i.e. 0(1). In the stoichiometric compound $YBa_2Cu_3O_6$ the formal charge of copper Cu(1) equals 1+, thus the occurrence of electron holes will be connected with the transition of copper into Cu^{2+} or the appearance of holes in the oxygen band /66,75-77/. The positive sign of thermoelectric power reported for this compound over a wide composition range /68-71, 78-82/ might support the above type of defect formation. The question now arises, similar to that in the previous example, to determine the pressure dependences of ionic and electronic defect concentrations on the basis of equilibrium constants of defect formation (Eqs. 35 and 37), and to compare thus obtained functions with the experimental ones. The mass action law applied to Eq. (35) results in:

$$K_{35} = a_{O_i''} a_h^2 / a_{V_i} P_{O_2}^{1/2} = [O_i''][h^{\cdot}]^2/[V_i]P_{O_2}^{1/2} \quad (38)$$

where a denotes activity of corresponding defects, [ ] - denote defect concentrations in mole/mole of the compound. In the oxide under consideration it is possible to assume that defect activity is approximately equal to its concentration (high value of dielectric constant /83/). The dependence of interstitial oxygen ion concentration on oxygen pressure is:

$$K_{35} = 4x^3/(1-x)P_{O_2}^{1/2} \quad (39)$$

where $[O_i''] = x$, $[h^{\cdot}] = 2x$, $[V_i] = 1-x$.

As follows from the above equation, the dependence of defect concentration on oxygen pressure is a complicated function. In order to compare the above dependence with others involving defects with a different degree of ionization, it is useful to analyze the dependence of $d\ln x/d\ln P_{O_2}$ on defect concentration. By differentiating Eq. 39 the following expression for the derivative is obtained:

$$n_{35}^x = d\ln P_{O_2}/d\ln x = 6 + 2x/(1-x) \quad (40)$$

Similarly, the equilibrium constant for the reaction (36) takes the form:

$$K_{36} = [O_i'][h^{\cdot}]/[V_i]P_{O_2}^{1/2} = x^2/(1-x)P_{O_2}^{1/2} \quad (41)$$

where $[O_i'] = x$, $[h^{\cdot}] = x$, $[V_i] = 1-x$.

In turn, the derivative $d\ln P_{O_2}/d\ln x$ is expressed by the equation:

$$n_{36}^x = d\ln P_{O_2}/d\ln x = 4 + 2x/(1-x) \quad (42)$$

The equilibrium constant for the reaction (37) is:

$$K_{37} = [O_i]/[V_i]P_{O_2}^{1/2} = x/(1-x)P_{O_2}^{1/2} \quad (43)$$

The corresponding equation for the derivative takes the form:

$$n_{37}^{x} = d\ln P_{O_2}/d\ln x = 2 + 2x/(1-x) \quad (44)$$

(Fig. 10) shows the dependence of $d\ln x/d\ln P_{O_2}$ on x. as can be seen, the derivative for different ionization degrees of the oxygen interstitials assumes different values and it changes with defect concentration.

Similarly, the equilibrium constant for the reaction of oxygen vacancy formation (Eq. 32) takes the form:

$$K_{32} = [V_O^{\cdot\cdot}]P_{O_2}^{1/2}/[h^{\cdot}]^2[O_O] = y\,P_{O_2}^{1/2}/(a_h-2y)^2(7-y) \quad (45)$$

where the concentration $[V_O^{\cdot\cdot}] = y$, $[O_O] = 7-y$, $[h^{\cdot}] = a_h - 2y$ (the parameter a_h denotes the maximum hypothetical concentration of the electron holes when y=0). By differentiating Eq. 45 the following expression for the derivative is obtained:

$$n_{32}^{y} = d\ln P_{O_2}/d\ln y = -2-8y/(a_h-2y)-2y/(7-y) \quad (46)$$

Similarly, the equilibrium constant for the reaction (33) is:

$$K_{33} = yP_{O_2}^{1/2}/(a_h-y)(7-y) \quad (47)$$

where $[V_O^{\cdot\cdot}] = y$, $[h^{\cdot}] = a_h - y$ and $[O_O] = 7-y$. In turn, the derivative $d\ln P_{O_2}/d\ln y$ is expressed by the equation:

$$n_{33}^{y} = d\ln P_{O_2}/d\ln y = -2-2y/(a_h-y)-2y/(7-y) \quad (48)$$

For Eq. 34 the equilibrium constant takes the form:

$$K_{34} = [V_O^{\cdot\cdot}][e']P_{O_2}^{1/2}/[h^{\cdot}][O_O] = y^2P_{O_2}^{1/2}/(a_h-y)(7-y)$$

where $[V_O^{\cdot\cdot}] = y$, $[h^{\cdot}] = a_h - y$, $[e'] = y$. The corresponding equation for the derivative is:

$$n_{34}^{y} = d\ln P_{O_2}/d\ln y = -4-2y/(a_h-y)-2y/(7-y) \quad (50)$$

As follows from Eqs. 46, 48 and 50, the $d\ln P_{O_2}/d\ln y$ derivative is a function of defect concentration. The values of the derivative for different defect structure models cannot be compared directly, since the a_h parameter is unknown. It is possible, however, to calculate this parameter for different models on the basis of known values of the derivatives.

As already mentioned, the dependence of the deviation from stoichiometry on oxygen pressure can be described in two ways, either by assuming the existence of oxygen vacancies ($YBa_2Cu_3O_{7-y}$) or oxygen interstitials ($YBa_2Cu_3O_{6+x}$). The two types of deviation from stoichiometry can be related as follows:

$$y = 1 - x \quad (51)$$

In accordance with the earlier discussion, the results presented in Fig. 9 determine the dependence of oxygen

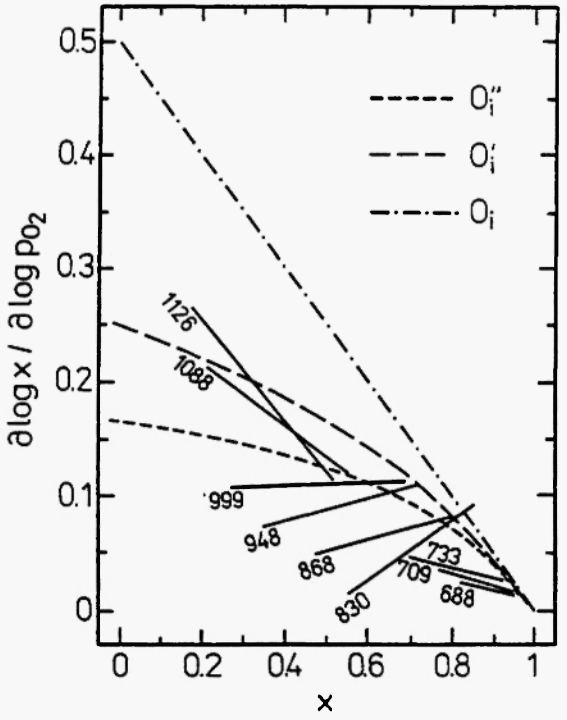

Fig. 10: The dependence of the derivative $d\log x/d\log P_{O_2}$ (Eqs. 40, 42 and 44) on non-stoichiometry x for oxygen interstitial ions of different ionization degree. Solid line - range of changes of the derivative obtained experimentally.

oxygen vacancy concentration on oxygen pressure /59/. Following the relation (51), Fig. 11 shows the same experimental results as the dependence of oxygen interstitial concentration on oxygen pressure.

In order to determine the type of defects dominating in different temperature and oxygen pressure ranges, the experimental dependences $\log x/\log P_{O_2}$ were analyzed. The experimental points were described with polynomials of second order and corresponding derivatives were calculated for different temperatures. Fig. 10 presents the variations of the derivatives for interstitial oxygen ions together with the theoretical curves representing the dependence of $d\ln x/d\ln P_{O_2}$ on x (Eqs. 40, 42, 44) for different defect types. As can be seen, the agreement between the experimental and theoretical values of the derivative $d\ln x/d\ln P_{O_2}$ for the considered defect types is satisfactory at the temperatures 1126 and 1088 K.

In the case when oxygen vacancies are assumed to be the predominant ionic defects, an analysis similar to that carried out for the interstitials is impossible since

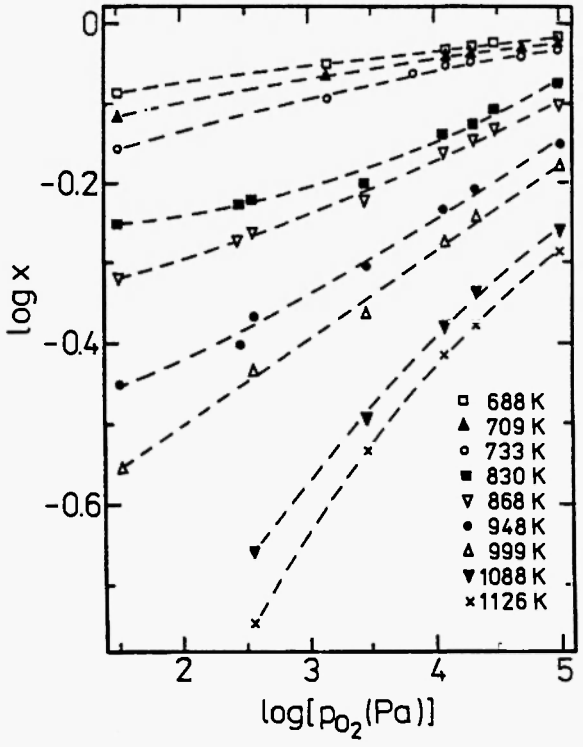

Fig. 11: The dependence of deviation from stoichiometry in $YBa_2Cu_3O_{6+x}$ on oxygen pressure at different temperatures.

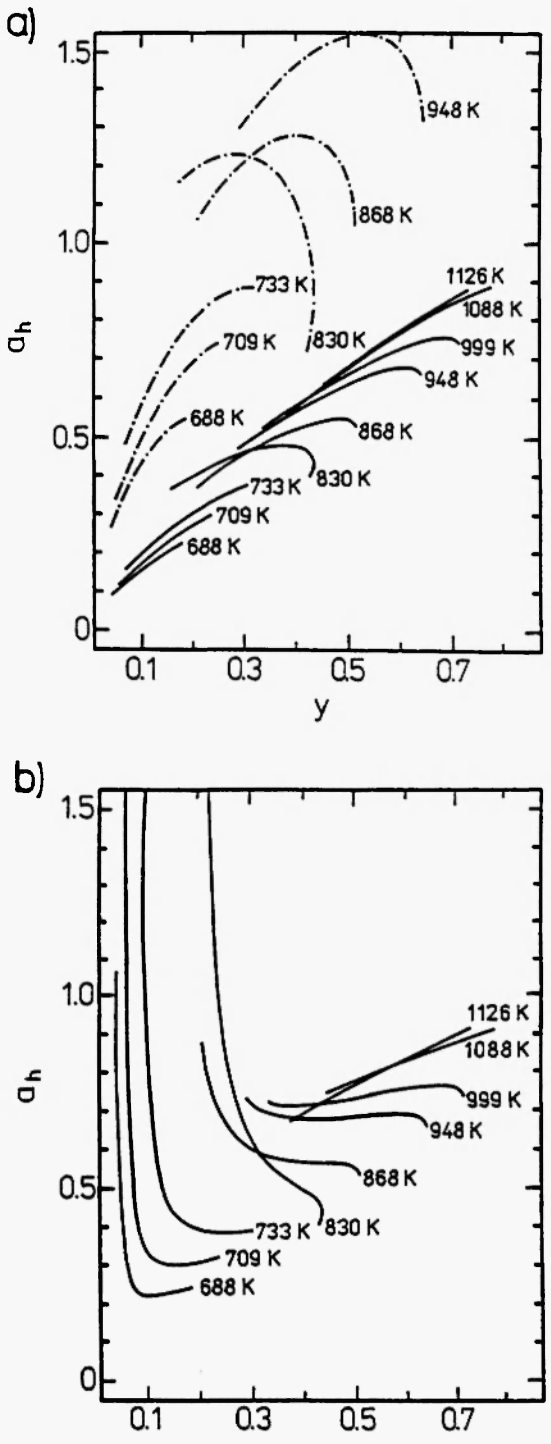

Fig. 12: The dependence of a_h parameters on non-stoichiometry y for different types of defects at different temperatures calculated on the basis of experimental values of $d\log y/d\log P_{O_2}$ and equations: a) Eq. 46 (- · - · -) and Eq. 48 (——), b) Eq. 50(——).

the concentration of electron holes at the stoichiometric composition remains unknown (unknown parameter a_h). It is possible, however, to calculate the a_h parameter from Eqs. 45, 47 and 49 and from the experimental values of $d\ln P_{O_2}/d\ln y$. The a_h parameter should fall in the range $0<a_h<1$, and at constant temperature it should not depend on defect concentration (oxygen pressure). Fig. 12 presents the dependence of a_h on oxygen vacancy concentration at each temperature. It can be stated that, for the model described with Eq. 32, reasonable values of a_h have been found merely for the lowest temperatures studied (690-730 K), strong dependence of a_h on defect concentration being observed. On the other hand, for the model described with Eq. 33, reasonable a_h values have been obtained in the whole temperature range studied, with a very weak dependence of a_h on defect concentration at the highest temperatures (950-1130 K) (Eq. 34).

Thus, it can be suggested that within the stability range of the orthorhombic phase the predominant defects should be singly and doubly ionized oxygen vacancies and electron holes, whereas for the tetragonal phase these should be singly ionized vacancies which upon ionization at higher temperatures produce free electrons. The proposed model of the defect structure has been fully confirmed by electrical properties examined under the conditions of thermodynamic equilibrium /72/.

This interpretation of experimental results indicates that it is difficult to decide which type of point defects dominates in each temperature and oxygen pressure range. The model involving "interstitials" might be accepted at the highest temperatures studied. The model assuming the existence of oxygen vacancies leads to much smaller discrepancies between the experimental results and theory.

7. CONCLUSIONS

The interpretation of thermogravimetric and electrical measurements for a number of highly nonstoichiometric compounds given in this paper enables us to draw the following conclusions:

- The examination of defect structure in nonstoichiometric compounds calls for simultaneous analysis of thermogravimetric and electrical measurements (the latter including electrical conductivity, thermoelectric power, etc.) carried out under conditions of thermodynamic equilibrium as a function of oxidant pressure. If the conclusions derived from such an analysis are consistent, a tentative model of defect structure can be proposed.
- Large deviations from stoichiometry imply a high concentration of electronic defects, complexity of band structure and finally charge transport in more than one energy band. Highly defective compounds generally exhibit a narrow energy gap, which can easily be overcome by thermally activated electrons giving rise to an intrinsic component of electrical conductivity. This component has to be taken into account, since otherwise the character of pressure dependence of electrical conductivity may be falsified (e.g. TiS_2, (Fe,Mn)O).
- Increasing deviation from stoichiometry brings about defect interactions due to which the ionization degree of defects decreases (TiS_2) or defect clusters are formed ((Fe,Mn)O).
- Defect equilibria in nonstoichiometric compounds can be described by equilibrium constants (mass action law) for the reactions of defect formation, without neglecting the activity coefficients.
- Different models of defect structure can be verified with the aid of a thermodynamic method, based on the mass action law and on analysis of the derivative of pressure dependence of defect concentration, especially in those cases for which the equilibrium constants of defect formation are not available or charged with big systematic errors.
- If ionic defects are present in more than one sublattice, then the pressure dependences of ionic and electronic defect concentrations may have a completely different character (examples Na_xCoO_2, $YBa_2Cu_3O_z$).
- The low precision of high-temperature thermogravimetric and electrical measurements as well as the fact that necessary activity coefficients are impossible to estimate disables full description of defect structure. Nevertheless, correct

interpretation of the experimental results makes it possible to determine the type of predominant defects.

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