

INTERNATIONAL UNION OF PURE AND APPLIED CHEMISTRY  
INORGANIC CHEMISTRY DIVISION  
COMMISSION ON HIGH TEMPERATURE MATERIALS AND SOLID STATE CHEMISTRY

# THERMODYNAMIC CHARACTERIZATION OF HIGH-TEMPERATURE SUPERCONDUCTORS IN THE YTTRIUM-BARIUM-COPPER-OXYGEN SYSTEM. THE Y123 SOLID SOLUTION

(Technical Report)

Prepared for publication by  
G. F. VORONIN

*Moscow State University, Department of Chemistry, 119899, Moscow, Russia*

Contributors: M. Chase (NIST, Washington, USA), K. Conder (ETH, Zürich, Switzerland), S. Degterov (Ecole Polytechnique, Montreal, Canada), J. Karpinski (ETH, Zürich, Switzerland), T. Lindemer (ORNL, Oak Ridge, USA), E. Rudnyi (Moscow State University, Moscow, Russia), G. Voronin (Moscow State University, Moscow, Russia).

Membership of the Commission during the period (1991–99) when this Report was prepared was as follows:  
*Chairman:* K. E. Spear (USA, 1998–99); G. M. Rosenblatt (USA, 1996–97); J. Corish (Ireland, 1989–95); *Secretary:* D. Kolar (Slovenia, 1996–99); G. M. Rosenblatt (USA, 1991–95); *Titular Members:* J.-F. Baumard (France, 1985–93); H.-P. Boehm (Germany, 1994–1999); J.-O. Carlsson (Sweden, 1996–99); C. B. J. Chatillon (France, 1998–99); J. D. Drowart (Belgium, 1987–93); L. N. Gorokhov (Russia, 1987–95); J. W. Hastie (USA, 1987–93); Meral Kizilyalli (Turkey, 1996–97); D. Kolar (Slovenia, 1994–99); J. Livage (France, 1996–99); M. H. Lewis (1996–99; UK, 1996–99); K. E. Spear (USA, 1998–99); G. F. Voronin (Russia, 1998–99); D.-S. Yan (China, 1987–95); *Associate Members:* G. Balducci (Italy, 1994–99); J.-F. Baumard (France, 1994–97); H. P. Boehm (Germany, 1991–93); A. V. Chadwick (UK, 1998–99); C. Chatillon (France, 1989–97); J. B. Clark (South Africa, 1985–91); L. N. Gorokhov (Russia, 1996–97); J. G. Edwards (USA, 1987–95); H. Hausner (Germany, 1987–91); L. H. E. Kihlberg (Sweden, 1985–91); Meral Kizilyalli (Turkey, 1996–95); R. Kniep (Germany, 1998–99); K. Koumoto (Japan, 1994–99); M. Leskela (Finland, 1998–99); M. H. Lewis (UK, 1989–99); C. M. Lieber (USA, 1998–99); B. Lux (Austria, 1996–99); J. Matousek (Czechoslovakia, 1985–93); H. J. Matzke (FRG, 1987–93); G. M. Rosenblatt (USA, 1985–91); T. Saito (Japan, 1989–93); K.E. Spear (USA, 1994–97); M. M. Thackeray (South Africa, 1991–95); G. van Tendeloo (Belgium, 1989–93); H. Verweij (Netherlands, 1996–99); G. F. Voronin (Russia, 1989–97); *National Representatives:* Noemi E. Walso de Reca (Argentina, 1994–1999); E. J. Baran (Argentina, 1985–91); P. Ettmayer (Austria, 1988–93); B. G. Hyde (Australia, 1987–93); J. D. Drowart (Belgium, 1994–99); M. Jafellicci, Jr. (Brasil, 1998–99); O. L. Alves (Brazil, 1991–93); E. Fitzner (Germany, 1986–93); J. Gopalakrishnan (India, 1998–99); C. K. Mathews (India, 1994–97); G. V. Subba Rao (India, 1989–93); G. De Maria (Italy, 1985–93); J. H. Chou (Korea, 1996–99); C. H. Kim (Korea, 1989–93); W.-L. Ng (Malaysia, 1989–93); K. J. D. MacKenzie (New Zealand, 1987–93); F. M. de Abreu da Costa (Portugal, 1991–93); F. Hanic (Slovakia, 1994–99); M. A. Alario Franco (Spain, 1987–93); Danita de Waal (South Africa, 1996–99); Meral Kizilyalli (Turkey, 1987–93); K. E. Spear (USA, 1989–93); D. Kolar (Slovenia, 1987–93).

---

*Republication or reproduction of this report or its storage and/or dissemination by electronic means is permitted without the need for formal IUPAC permission on condition that an acknowledgment, with full reference to the source, along with use of the copyright symbol ©, the name IUPAC, and the year of publication, are prominently visible. Publication of a translation into another language is subject to the additional condition of prior approval from the relevant IUPAC National Adhering Organization.*

# Thermodynamic characterization of high-temperature superconductors in the yttrium-barium-copper-oxygen system. The Y123 solid solution

*Abstract:* The aim of this report is to inform the chemical community about a self-consistent thermodynamic data set for the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+z}$  ( $1 \geq z \geq 0$ ) solid solution, that is well known as the Y123 phase and possesses superconducting properties at  $z \sim 1$  and low temperatures. About 3300 experimental points obtained in 240 miscellaneous experiments published in 78 papers have been processed simultaneously in order to obtain the most reliable Gibbs energy function of the Y123 phase in the temperature range from 250 to 1300 K and pressures up to 100 kbar. A function is recommended for approximation of the Gibbs energy, which has 16 adjustable parameters. All other thermodynamic properties of the Y123 solution, including the conditions for its internal stability, can be derived from the assessed Gibbs energy. Brief descriptions of the thermodynamic model, experimental and data assessment methods as well as examples of self-consistent thermodynamic data applications are given.

## INTRODUCTION

The solid solution of oxygen in the compound  $\text{YBa}_2\text{Cu}_3\text{O}_6$  can be described by the formula  $\text{YBa}_2\text{Cu}_3\text{O}_{6+z}$ , where the oxygen index  $z$  varies from 0 to 1. The usual abbreviation for this formula is Y123. The Y123 phase is the base of the first material that has been found to be superconducting at about the liquid nitrogen temperature [1]. At present it is considered to be the high-temperature superconductor that is most likely to be used in technical application. This phase was found to exist in two crystal structures, tetragonal and orthorhombic. Only the latter happened to be a superconductor: the higher oxygen content and ordering in the crystal lattice, the better are superconducting properties of the Y123 material.

Thermodynamic calculations confirmed by some special experiments strongly suggest that the superconducting Y123 phase exists as a metastable phase only and that it can spontaneously transform to other more stable phases [2,3,80,81]. That peculiarity and the existence of many other phases with a similar qualitative composition complicate experimental investigations of this superconductor. Therefore, it is of special importance to have available a theoretical prediction of suitable conditions for synthesis and the use of this material and in particular, thermodynamic calculations of its stability at different temperatures, composition, and pressures, in the presence of other materials and gases. A set of data that is sufficient for the calculation of stability and interactions is provided by the Gibbs energy functions of the main phases in the Y-Ba-Cu-O system. When the Gibbs energy function is known all the other thermodynamic properties of phases and their internal stability conditions can be obtained by means of well-known thermodynamic relations.

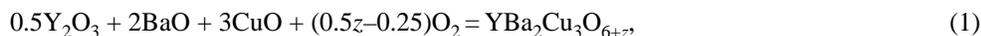
In this report all experimental investigations related to the thermodynamic properties of the solid Y123 phase and the determination of its most reliable Gibbs energy function are reviewed. Publications exist in which the Gibbs energy function is obtained to a rough estimation only, on the basis of the measured enthalpy of formation, for example [67,70,74]. Unfortunately, the system of interest is too complicated to expect any significant progress by following this approach.

Reviews on the thermodynamics and phase diagrams of the Y-Ba-Cu-O system, can be found in Refs. [45,80,82–84].

## THERMODYNAMIC MODEL

The model has to present the dependence of the thermodynamic properties as a function of all its state variables. There are many attempts to use detailed models for description of the properties or the results of individual experiments with the Y123 phase, such as a temperature of transition between tetragonal and orthorhombic crystal phases, variation of the oxygen content with oxygen partial pressure and temperature, heat capacities with temperature, etc. [4,5,7]. This approach accounts for the particular phase behavior, but cannot be used for determination of data for thermodynamic equilibrium calculations, which need an appropriate characteristic function, such as the Gibbs energy. Moreover, employment of several detailed models for description of one complete substance usually leads to discrepancies, because of the existence of rigorous interrelations between all thermodynamic properties. Hence, step-by-step consecutive interpretation of heat capacity, enthalpy, oxygen content, and other properties of the Y123 phase without employing any overall description results in equations that do not obey the thermodynamic laws [7,68]. In Ref. [6] a general description of the Y123 phase thermodynamics is claimed, but without any concrete data or references to publications of appropriate results.

A complete thermodynamic description of the Y123 Gibbs energy function has been developed on the basis of a sublattices model in Refs. [2,8–12]. The proposed model accounts for the existence of two crystal modifications, their reciprocal transformation by means of the second order phase transition, oxygen solubility in the range  $1 \geq z \geq 0$ , oxygen occupancies and ordering in the basal plane of the crystal lattice, and the effect of temperature, composition, and pressure on the thermodynamic properties of the phase. The expression obtained for the Gibbs energy of formation of the Y123 phase from the oxides,  $Y_2O_3$ , BaO, CuO, and oxygen, i.e., the Gibbs energy of the reaction



is as follows [12]:

$$\begin{aligned} \Delta_{\text{ox}}G(T,P,z,x)/R = & g_1(T,P) + g_2(T,P) \cdot z + z \cdot (1-z) \cdot \sum_{i=1} a_i(T,P) \cdot (1-z)^{i-1} \\ & + (c^2 - x^2) \cdot \sum_{i=1} b_i(T,P) \cdot (1-z)^{i-1} + [(c+x) \cdot \ln(c+x) + (c-x) \cdot \ln(c-x) \\ & + (1-c+x) \cdot \ln(1-c+x) + (1-c-x) \cdot \ln(1-c-x) + z \cdot \ln z + (1-z) \cdot \ln(1-z)] \cdot T, \end{aligned} \quad (2)$$

where  $z$  is the oxygen index ( $1 \geq z \geq 0$ ),  $c$  is short for  $z/2$ ,  $x$  is the oxygen order parameter describing oxygen distribution in the basal plane of the crystal lattice ( $z/2 \geq x \geq 0$ ),  $R$  is the gas constant. The temperature  $T$  and pressure  $P$  dependent functions  $g_i(T,P)$ ,  $a_i(T,P)$  and  $b_i(T,P)$  have identical equation

$$\begin{aligned} r_i(T,P)/K = & A_{ri} + B_{ri} \cdot (T/K) + C_{ri} \cdot (T/K) \cdot \ln(T/K) + D_{ri} \cdot (T/K)^{0.5} \\ & + W_{ri} \cdot \exp[\lambda_{ri} \cdot (T/K)] \cdot \{1 - \exp[\varphi_{ri} \cdot (1 - P/P^0)]\} / \varphi_{ri} \end{aligned} \quad (3)$$

( $r = g, a, \text{ or } b$  and  $i = 1, \dots$ ) and various parameters  $A_{ri}/K$ ,  $B_{ri}$ ,  $C_{ri}$ ,  $D_{ri}/K^{0.5}$ ,  $W_{ri}/K$ ,  $\lambda_{ri}/K^{-1}$ ,  $\varphi_{ri}$ , that are fit to experimental data.  $P^0$  - reference pressure equals to 101 325 Pa. Equations (2,3) are obtained for use in the temperature range from 250 to 1300 K and  $P/P^0$  up to 100 000.

The model allows for differing occupations of oxygen sites in the two sublattices to accommodate the Gibbs energy for tetragonal and orthorhombic modifications. To this end, the order parameter  $x$  in (2) is defined as the difference between the oxygen occupancies  $y_O$  in the sublattices (b) and (a) as follows [2]

$$x = (y_O^{(b)} - y_O^{(a)})/2 = z/2 - y_O^{(a)}, \quad (4)$$

where oxygen occupancy  $y_O$  means the oxygen mole fraction in the corresponding sublattice (a) or (b). Accordingly,  $1 - y_O$  gives the mole fraction of vacant sites. Thus,  $x$  should be equal to zero for the tetragonal phase and  $z/2 > x \geq 0$  for the orthorhombic phase. The equilibrium value of  $x$  at any given  $T$  and  $z$  can be determined by minimizing (2) over order parameter  $x$ , or by equating to zero the partial

derivative of  $\Delta_{\text{ox}}G$  with respect to  $x$

$$(\partial\Delta_{\text{ox}}G/\partial x)_{T,z} = 0. \quad (5)$$

Sometimes, in quenched samples for instance, the order parameter might not reach an equilibrium value. If that is the case, the order parameter can be used immediately in (2), if it is known.

The phase border between two crystal modifications can be found by solving the following equation, that is the thermodynamic condition for the second-order phase transition:

$$(\partial^2\Delta_{\text{ox}}G/\partial x^2)_{T,z}|_{x=0} = 0. \quad (6)$$

This equation allows us to compute the phase transition temperature at the given index  $z$  provided all the parameters for (2) are known. The equilibrium oxygen partial pressure  $p$  over the Y123 solid solution can be calculated from

$$RT \cdot \ln(p/P^0) = 2 \cdot [\partial\Delta_{\text{ox}}G(T,z,x)/\partial z]_{T,x} \quad (7)$$

All other thermodynamic properties can be obtained by means of well-known thermodynamic relationships. For instance, a formula for calculation of the molar volume  $V_m$  follows from (2) as derivative of  $\Delta_{\text{ox}}G$  with respect to  $P$ :

$$\begin{aligned} P^0 \cdot V_m(T,P,z,x)/R = & W_{g1} \cdot \exp[\lambda_{g1} \cdot T + \phi_{g1} \cdot (1 - P/P^0)] + z \cdot W_{g2} \cdot \exp[\lambda_{g2} \cdot T + \phi_{g2} \cdot (1 - P/P^0)] \\ & + z \cdot (1 - z) \cdot \sum_{i=1} W_{ai} \cdot \exp[\lambda_{ai} \cdot T + \phi_{ai} \cdot (1 - P/P^0)] \cdot (1 - z)^{i-1} \\ & + (c^2 - x^2) \cdot \sum_{i=1} W_{bi} \cdot \exp[\lambda_{bi} \cdot T + \phi_{bi} \cdot (1 - P/P^0)] \cdot (1 - z)^{i-1}. \end{aligned} \quad (8)$$

The product of  $V_m$  and  $P$  expresses the thermal equation of states for the Y123 phase.

## EXPERIMENTAL INVESTIGATIONS

Table 1 summarizes available information on direct experiments that allow the thermodynamic properties of the Y123 phase at temperatures  $\geq 250$  K to be determined. At the first column of this table the groups of experiments are classified according to the measured property and variables under control. More detailed descriptions for the classification method are given in Ref. [8] and for experiments - in Refs. [2,8,12,13,80]. There are many other publications with results of indirect measurements of the Y123 thermodynamic properties such as the investigation of the Y123 decomposition reactions. However, to be able to interpret these results the properties of other compounds or solutions in the Y-Ba-Cu-O system are required, and hence for this reason these results are not considered in Table 1.

### Phase transitions and oxygen occupancies

In a typical experiment an Y123 sample was heated or cooled in a controlled atmosphere with a known oxygen partial pressure. The transitions between orthorhombic and tetragonal phases were detected by a bend in the TGA or resistivity curve, or by X-ray diffraction methods. The experiments carried out by Refs. [14,15] were quite similar except that the oxygen partial pressure was not fixed during the heating/cooling cycle. One problem is that the authors have presented not the original experimental values of  $p$  but rather recalculated values at the index  $z$  according to their own measurements. Thus, here experimental points are given in the form  $T_{\text{tr}}(p)$  or  $T_{\text{tr}}(z)$  (see Table 1).

The oxygen occupancies in the sublattices (a) and (b) (see (4)) have been measured in Refs. [16,17]. Neutron diffraction has been employed in the first work and profile fitting of X-ray diffraction reflections in the second. The experiments were carried out at constant oxygen partial pressure and at several temperatures, and the experimental points look like  $x(T, p)$ .

**Table 1** Experimental results available for assessment of the Y123 phase properties

| Measurements                        | $N^a$ | Methods <sup>b</sup> | References                |
|-------------------------------------|-------|----------------------|---------------------------|
| $T_{tr}(p)^c$                       | 42    | XRD, TGA, RES        | 30–32, 46–54              |
| $T_{tr}(z)$                         | 20    | RES                  | 14, 15                    |
| $x(T, p)$                           | 39    | NDA, XRD             | 16, 17                    |
| $z(T, p)$                           | 583   | NDA, TGA, CHA        | 16, 17, 18, 30–32, 55–60  |
| $p(T, z)$                           | 1553  | VLA, EMF, TGA        | 15, 18, 20, 30, 31, 61–66 |
| $p(T, v)^d$                         | 681   | MPM                  | 19                        |
| $\Delta_{ox}H_O(873\text{ K}, z)^e$ | 19    | SCL                  | 20                        |
| $\Delta_{ox}H(T, z)$                | 51    | SCL                  | 21, 69–78                 |
| $S(298\text{ K}, z)$                | 6     | ACL                  | 86–89                     |
| $C_p(T, z)$                         | 108   | ACL, DSC             | 23, 24, 85–89             |
| $\Delta_{ox}G(T, p)$                | 28    | EMF                  | 26–28                     |
| $V_m(298\text{ K}, z)^f$            | 85    | XRD                  | 14, 17, 18, 21, 32, 35    |
| $V_m(T, p)$                         | 132   | NDA, XRD             | 16, 30, 31, 34            |
| $V_m(298\text{ K}, P, z)$           | 57    | XRD                  | 36, 37, 39                |

<sup>a</sup> $N$  - total number of experimental data points.

<sup>b</sup>see a list of acronyms.

<sup>c</sup> $p$ - oxygen partial pressure,  $T_{tr}$ - temperature of transition between two crystal structures.

<sup>d</sup> $v$  - volume of the gas oxygen equilibrated with the Y123 phase at given total pressure,  $P$ .

<sup>e</sup> $\Delta_{ox}H_O$  - relative oxygen partial enthalpy of the Y123 phase.

<sup>f</sup> $V_m$  - molar volume of the solid Y123 phase.

## Oxygen partial properties

Unfortunately, many results in this group of experiments are available only in graphic form. In most experiments, the relationship between the oxygen partial pressure over the Y123 phase, index  $z$ , and temperature has been studied. There are many approaches to study this two-dimensional surface, and it seems that all of them have been implemented in the case of the Y123 phase.

It is rather simple to control the oxygen partial pressure over the Y123 phase. Thermogravimetry allows us to measure the weight of the sample as a function of temperature and thus to measure the dependence of the index  $z$  on temperature at constant oxygen partial pressure. This gives experimental points in the form  $z(T, p)$ . Another approach is to study isotherms; that is, the dependencies of  $p(T, z)$ . The techniques employed were the EMF method, volumetric apparatus, and TGA. The same functions are obtained in Ref. [18,92], where a special apparatus based on the volumetric approach to maintain a constant the value of index  $z$  while heating or cooling the Y123 was used. The work of Ref. [15] is also included in this group even though the real experimental conditions were not isothermal, because the results of publication are available in the isothermal form only.

In Ref. [19] the traditional volumetric experiment was implemented but with a different experimental path. The total pressure was measured as a function of temperature at constant total volume. After assuming that the gas phase contains molecular oxygen only, the experimental points were obtained as  $p(T, V_c, z_i^o, m_i^o)$ , where  $V_c$  is the volume of the chamber,  $z_i^o$  is the index, and  $m_i^o$  is the mass of the original sample. During the experiment, the index  $z$  changed because some oxygen escaped from  $\text{YBa}_2\text{Cu}_3\text{O}_{6+z}$  to the gas phase. Assuming that molecular oxygen obeys the perfect gas law and neglecting the volume of the condensed phase, the current index  $z$  can be calculated [12]. In Table 1 this approach is classified under the  $p(T, v)$  experimental group.

Oxygen partial enthalpies have been measured by reaction microcalorimetry in Ref. [20] as a function of the index  $z$  at 873 K. Authors of Ref. [21] have also employed high-temperature reaction

calorimetry; however, the experiment was carried out differently, and the results here are available as transposed-temperature-drop enthalpy measurements [12].

### Integral properties

The measured thermodynamic properties discussed so far would be enough to predict the behavior of the Y123 phase by itself even though they do not allow us to estimate the temperature function  $g_1(T,P)$  in (2) because it disappears during the differentiation with respect to index  $z$ . Yet, in order to predict results of the interaction with other substances one has to know the Gibbs energy as a whole. To this end, experiments are available where the integral Gibbs energy, the enthalpy, the entropy and the heat capacity have been measured.

Oxygen adsorption and desorption from the Y123 phase below  $\approx 450$  K can be considered as kinetically fully hampered ("frozen") and the index  $z$  at these temperatures cannot be controlled anyway by the external oxygen partial pressure. This allows us to obtain the heat capacity as a function of temperature at constant  $z$ . The experimental data are presented as  $C_p(T, z)$ . All the available values are divided into two groups: low-temperature heat capacity measured by adiabatic calorimetry and high-temperature heat capacity measured by differential scanning calorimetry.

The low-temperature heat capacity measurements are characterized by rather good accuracy, and the results are usually available in the temperature range from liquid helium to room temperature. Because of the limitations in the temperature range used, description of the heat capacity in (2) was possible only above 250 K. Accordingly, the results of adiabatic calorimetry were considered as two different types of measurements, the absolute entropy at 298.15 K, estimated as an integral over all the temperature range, and the upper part of the heat capacity curve ( $T > 250$  K). The precision of the heat capacity measured by DSC is not as good as from adiabatic calorimetry. Another problem is that at higher temperatures oxygen adsorption/desorption can occur, and interpretation of the results becomes rather difficult (see discussion in Ref. [22]). This was the reason only high-temperature heat capacities below 425 K were considered here. In the original studies [23,24], the results are available up to 900 K.

The changes of enthalpies and Gibbs energies are given for reaction (1). The enthalpy of formation of the Y123 phase has been measured in a number of laboratories by means of solution calorimetry and, as one may expect, there is a great scatter among the results. Authors of Ref. [25] have thoroughly reviewed calorimetry results and pointed out that the main problem responsible for the scatter between different laboratories is due to impurities of the oxides used for calorimetry (especially BaO that reacts readily with H<sub>2</sub>O and CO<sub>2</sub> from the air). If the authors have not paid attention to the purity of the samples, or at least if this question is not discussed in the paper, their results are less reliable than from those who have carefully discussed this problem. Numerical results for the assessment were taken from [25], where almost all results have been recalculated with the same set of auxiliary values.

There are a few papers, giving EMF measurements of the Gibbs energy of formation from oxides [26–28]. Because of the high-temperature nature of the method, the results are available at fixed oxygen partial pressure, i.e., in the form of  $\Delta_{\text{ox}}G(T, p)$ . Only the results of [28] are in reasonable agreement with calorimetric enthalpies and entropies. The authors of Ref. [2] have discussed the various studies and suggested that the disagreement in the case of [26,27] can be explained by ambiguities in auxiliary values that are necessary to recalculate the experimental values for reaction (1). As a result, only Ref. [28] was used, and two other studies are put into the group of unreliable experiments.

### Volume and elastic properties

Some of the experiments mentioned above were done with the Y123 phase at a total pressure deviating from  $P^0$ . Expression (2) allows for the effect of hydrostatic pressure on the thermodynamic properties of phase, but for an accurate determination of the parameters  $W_{r_i}$ ,  $\lambda_{r_i}$  and  $\varphi_{r_i}$  in (3), volume measurements

at different  $T$  and  $P$  are needed. These data were usually calculated from the values of the crystal lattice parameters determined by means of XRD [14,17, 18,21,30–35] or NDA [16]. From these results crystal thermal expansion coefficients, compressibility, or bulk modulus can be also derived. There is evidence for some anisotropy in the elastic properties of the Y123 phase. This behavior can be observed with single crystals, but not on the ceramic samples. In particular, the latter are the object of description by the model (2), in which  $P$  is the hydrostatic pressure. Therefore, the values of the elastic property resulting from the accepted model are the mean quantities of the same property for different crystallographic axes.

XRD permits study of the specimen at high static pressure generated directly with diamond anvils [36–38] or by a liquid pressure-transmitting medium [39,40]. Some published investigations of the Y123 phase elastic constants were not used for the assessment because of too low temperatures [29]. Likewise measurements of sound velocity and attenuation in ceramic specimens were not used as they gave results depending on the uncontrolled porosity of the samples [41].

### DATA ASSESSMENT METHOD

The task of simultaneous assessment is to obtain a set of parameters in (2, 3) that gives the best description of the original experimental values, described briefly in Table 1, provided that thermodynamic properties of the pure oxides and oxygen are known (see Table 2). The relationship between the measured property  $f_{ij}$  and the same property calculated by thermodynamic laws at given controlled thermodynamic variables  $u_{ij}$ ,  $v_i$  and the vector of unknown parameters  $\theta$  in (2) can be expressed in the general form as

$$f_{ij} = f_{ij}^{\text{calc}}(u_{ij}, v_i, \theta) + \varepsilon_{ij} \quad (9)$$

where index  $j$  denotes the experimental points within the  $i$ -th experiment (the group of measurements made with the same sample on the same equipment),  $\varepsilon_{ij}$  is the experimental error.

All calculated thermodynamic properties of the  $\text{YBa}_2\text{Cu}_3\text{O}_{6+z}$  phase,  $f_{ij}^{\text{calc}}$ , could be obtained from (2) by means of algebraic and/or numerical methods. This means that the vector  $\theta$  contains the same set of unknown parameters for all the equations describing thermodynamic properties, although some parameters may vanish during differentiation of (2). So, for the experiments on the tetragonal-orthorhombic phase transformation  $f_{ij}$  in (9) is the temperature of the transformation at a given oxygen partial pressure,  $T_{\text{tr}}(p)$ , or composition,  $T_{\text{tr}}(z)$  (see Table 1). Values of  $T_{\text{tr}}^{\text{calc}}(p)$  can be obtained by solving the system of two equations (6) and (7) for two unknowns  $z$  and  $T$ , and  $T_{\text{tr}}(z)$  – by solving (6) for the unknown  $T$ . The next group of experiments in Table 1, equilibrium values of the oxygen occupancies, is computed by numerical solving the system of (5) and (7) for  $z$  and  $x$ , and so on.

The main problem in solution of a set of equations (9) lies in the question of what should be considered the best description of the experimental points. In other words, it lies in considerations of the uncertainties  $\varepsilon_{ij}$ . If all the errors  $\varepsilon_{ij}$  are postulated to be non-correlated random errors, and ratios between variances for all the errors are known *a priori*, the mathematical statistic leads us to the conventional approach of the weighted least squares method (WLS). But, both these statements are too restrictive for real-life applications. The variance ratios for experimental points are not known *a priori* and this makes a proper choice of statistical weights for the WLS calculation ambiguous. Then, as a rule, discrepancy between the results of different experiments is greater than data scatter within a single experiment (the ratio of the corresponding sum of squares is more than Fisher's criterion allows). This is explained in terms of experimental systematical errors. An appropriate statistical model for experimental errors was proposed in Refs. [42,43]. According to this approach  $\varepsilon_{ij}$  in (9) is replaced by the sum of tree errors:

$$\varepsilon_{ij} = \varepsilon_{r,ij} + \varepsilon_{a,i} + \varepsilon_{b,i}[u_{ij} - (\sum_j u_{ij})/N_i], \quad (10)$$

where the first one,  $\varepsilon_{r,ij}$ , is the random reproducibility error, and two others describe systematical errors

**Table 2** Thermodynamic properties of oxides and oxygen employed in the calculations (according to Ref. [79])<sup>a)</sup>.

| Component                                      | Y <sub>2</sub> O <sub>3</sub> | BaO       | CuO       | O <sub>2</sub> |
|--|-------------------------------|-----------|-----------|----------------|
| $\Delta_f H_{298}^\circ / (\text{J mol}^{-1})$ | -1919400                      | -548000   | -161700   | 0              |
| $A / (\text{J mol}^{-1})$                      | -30047.83                     | -5092.968 | -5669.132 | -1776.280      |
| $B / (\text{J mol}^{-1} \text{K}^{-1})$        | 954.1052                      | 463.41195 | 477.64762 | 132.54252      |
| $C / (\text{J mol}^{-1} \text{K}^{-1})$        | -146.996                      | -72.028   | -69.785   | -44.978        |
| $D / (\text{J mol}^{-1} \text{K}^{-0.5})$      | -2120.104                     | -1858.564 | -1801.184 | -1294.168      |
| $E / (\text{J mol}^{-1} \text{K})$             | 737146.5                      | 0         | 61609     | 0              |
| $F / (\text{J mol}^{-1} \text{K}^2)$           | -12441857                     | -9963433  | 0         | -13651002      |

<sup>a)</sup> The parameters from  $A$  to  $F$  in equation  $G^\circ(T) / (\text{J mol}^{-1}) = A + B(T/\text{K}) + C(T/\text{K}) \ln(T/\text{K}) + D(T/\text{K})^{0.5} + E(T/\text{K})^{-1} + F(T/\text{K})^{-2}$  for computation of function  $G^\circ(T) - \Delta_f H_{298}^\circ$  in the temperature interval from 250 to 1300 K,  $G^\circ(T)$  and  $\Delta_f H_{298}^\circ$  – standard Gibbs energy at temperature  $T$  and standard enthalpy of formation at 298.15 K.

for the  $i$ -th experiment. Values of  $\varepsilon_{a,i}$  accounts for the shift systematic error and  $\varepsilon_{b,i}$  for the tilt laboratory factor. The values of both systematic errors are constant within a single experiment, but they can change randomly among different experiments.

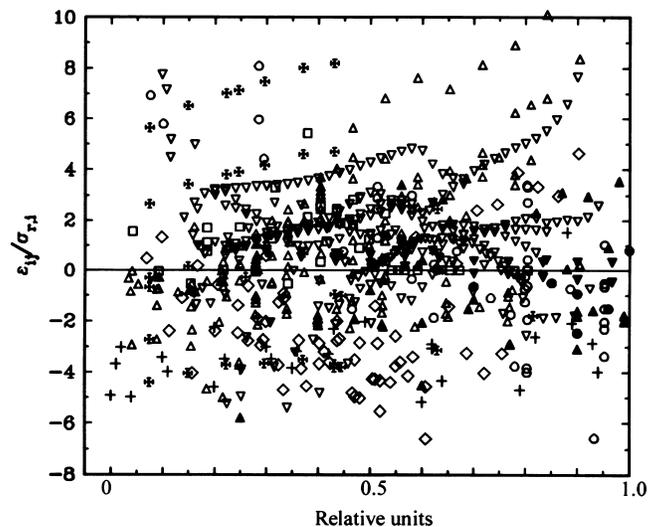
In the final formulation of the present task 16 unknown parameters from the Gibbs energy function (2, 3) plus 11 unknown variance components were used. The variance components are the variances of the errors in (9, 10). The number of unknown variances has been chosen under the principle of like compromise when the experiments have been divided into the groups possessed by the same quality (see details in [8]). Preliminary expert analysis and data assessment shows the existence of several groups of experiments that can be classified as “wrong” (see section 3 and Refs. [8,12]). Although these works are included in Table 1, their results are excluded from the final assessment. The complete set of equations (9) was solved by the maximization of the likelihood function [8,42,44]. The data optimization procedure for the Y123 phase is described in more details in Refs. [8,12].

The data assessment method used here has several practical advantages compared with conventional WLS. It allows us to exclude the adoption of the statistical weights of the experimental data when they are uncertain, it gives a real estimate for the variances of the fitting parameters, and it permits one to have a new look on the graphical comparison of the initial data. Figure 1 shows deviates normalized to the standard deviation for all experimental points included into the assessment for Y123 phase [8]. Obviously the total deviations exceed the reproducibility error by several times, which demonstrates the existence of systematic errors for the individual experiments.

### SELF-CONSISTENT DATA

The final values of the parameters assessed in (2,3) and their standard deviations are presented in Table 3. The results of data optimization show that parameters describing pressure dependence of the thermodynamic functions in (2,3), i.e.  $W_{g1}$ ,  $W_{g2}$ ,  $\lambda_{g1}$ , and  $\varphi_{g1}$ , are practically not correlated with the other parameters [12]. Therefore, the thermodynamic calculations in the case when the total pressure is less than 100 to 200 bar can be done without noticeable errors assuming these parameters to be zero. It is notable, that at zero values of  $\lambda_{ri}$  and  $\varphi_{ri}$  the last addends in (3) are  $W_{ri} \cdot (P/P^0 - 1)$ .

Figures 2 and 3 show examples of the description of the primary experimental points by the recommended self-consistent data. Other verifications of the model and comparison with experimental data are in Refs. [2,8,12,22,45].



**Fig. 1** Deviations of included into assessment experimental data points normalized to the standard deviation versus character variable of the appropriate experiment normalized to its maximal value. Single points represent data of measurements. A set of measurements in the same experiment has got its own symbol. After Ref. [8].

**Table 3** Parameters obtained within (2, 3) for the Y123 phase<sup>a</sup>.

| Parameters            | $r = g$                           | $r = a$            | $r = b$           |
|-----------------------|-----------------------------------|--------------------|-------------------|
| $A_{r1}/K$            | $-3564 \pm 541$                   | $2000 \pm 165$     | $652.1 \pm 164$   |
| $A_{r2}/K$            | $-10360 \pm 160$                  | $-2590 \pm 224$    | 0                 |
| $B_{r1}$              | $-4.918 \pm 0.490$                | $-1.544 \pm 0.204$ | $3.921 \pm 0.193$ |
| $B_{r2}$              | $45.99 \pm 4.59$                  | $4.044 \pm 0.279$  | 0                 |
| $C_{r2}$              | $-4.051 \pm 0.518$                | 0                  | 0                 |
| $D_{r2}/K^{0.5}$      | $-252.3 \pm 33.7$                 | 0                  | 0                 |
| $W_{r1}/K$            | $1.281 \pm 0.003$                 | 0                  | 0                 |
| $W_{r2}/K$            | $-0.02857 \pm 0.00213$            | 0                  | 0                 |
| $\lambda_{r1}/K^{-1}$ | $(4.230 \pm 0.306) \cdot 10^{-5}$ | 0                  | 0                 |
| $\phi_{r1}$           | $(8.122 \pm 0.728) \cdot 10^{-7}$ | 0                  | 0                 |

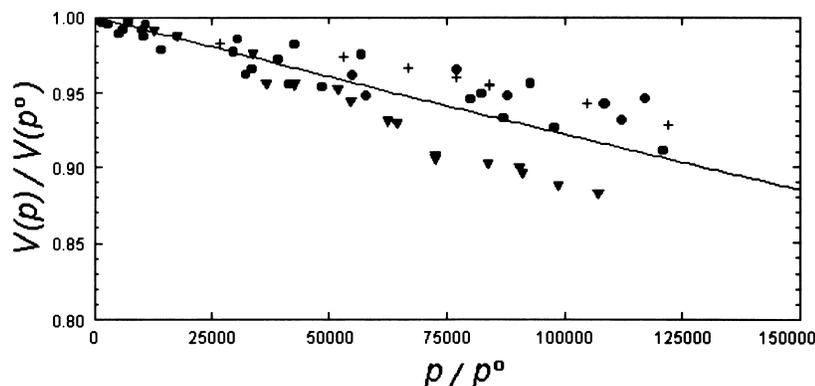
<sup>a</sup>The values of all parameters not included in the table are equal zero.

## SOME APPLICATIONS

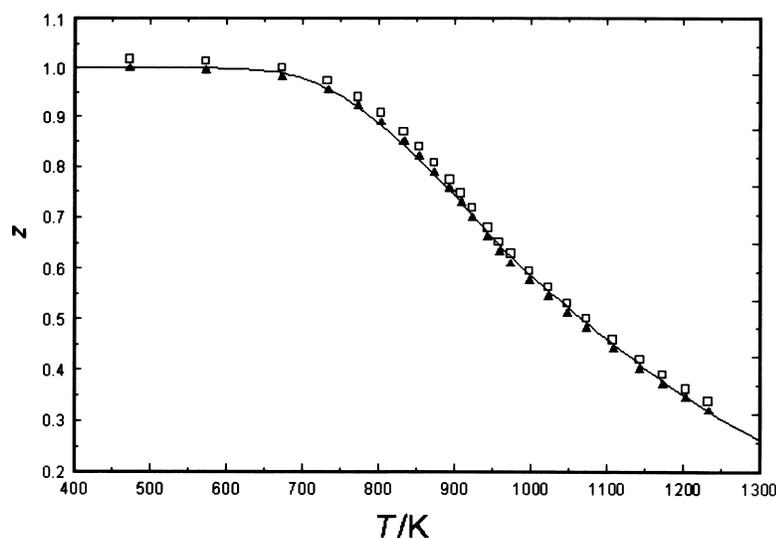
The main applications of thermodynamics are found in the use of databases that contain thermodynamic functions for many substances. The more substances and self-consistent data are accommodated the better become the possibilities for applications. Such employment of thermodynamics for the Y-Ba-Cu-O system can be found in Refs. [2,45,80,82]. Below examples concerning accepted Y123 solid solution data only are presented.

### Low-temperature decomposition

According to thermodynamics the Y123 solid solution cannot exist at very low temperatures. There are two possibilities for its conversion—splitting into two other solid solutions, which transform to the

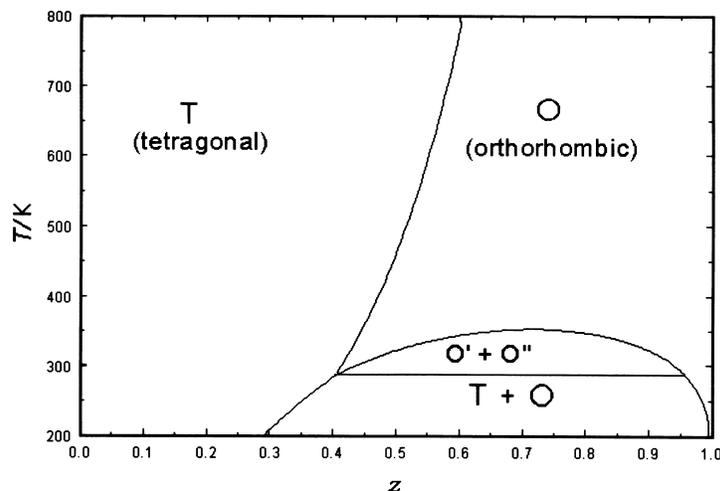


**Fig. 2** Relative volume of the Y123 phase versus hydrostatic pressure. Data points from experiments in Refs. [36,37,39] are represented by different symbols. After Ref. [12].



**Fig. 3** Thermogravimetric measurements of the oxygen content in the Y123 phase at  $\lg(p/P^0) = -0.05$  and various temperatures from Ref. [92]. Values of  $z$  were calibrated by the oxygen stoichiometry at 200 °C as determined by the weight loss after complete reduction of sample (squares) and by using the assumption that  $z$  equals 0.999 at 200 °C (triangles). The line was calculated from (7).

components as the temperature decreases, and ordering with formation of individual intermediate compounds. The first way is shown in Fig. 4. It should be implemented if the ordered intermediate phases are thermodynamically unstable, or if their formation is kinetically suppressed (for example, from over a big phase nucleation barrier). It seems that formation of ordered compounds from the Y123 phase is confirmed in several experiments [33,90,91]. Such being the case, Fig. 4 corresponds to the virtual metastable state decomposition of the Y123 solid solution. There is also some experimental evidence for the occurrence of this miscibility gap [64].



**Fig. 4** Calculated decomposition and phase transformation of the Y123 solid solution. After Ref. [8].

### Phase transition under pressure

Another question is how the relative stability of the orthorhombic and tetragonal Y123 structures varies with pressure. In Ref. [36] the orthorhombic to tetragonal transition was found only at pressures above 70 000 bar in contrast to other publications. Apparently, it was an irreversible transition, since an abrupt change of volume was observed. That points towards a first order rather than a second order transition. According to (2) or (8), because of the difference in the oxygen order parameter  $x$ , two structures have different stability at  $P$  unequal to  $P^0$  if at least one of the  $W_{bi}$  coefficients is not equal to zero. According to Table 3, the thermal equation of state for the Y123 is follows,

$$\begin{aligned} [P \cdot V_m(T, P, z, x)/R]/K = & \{ (W_{g1}/K) \cdot \exp[(\lambda_{g1}/K^{-1}) \cdot (T/K)] \\ & + \varphi_{g1} \cdot (1 - P/P^0) \} + z \cdot (W_{g2}/K) \cdot (P/P^0). \end{aligned} \quad (11)$$

The same is true for the both crystal modifications, which implies independence of their stability from the pressure. But, this conclusion should be considered as preliminary, because the available experimental data do not allow us to obtain a significant estimate for the  $W_{bi}$  parameters. This however does not exclude the possibility of this effect in principle. The final decision can be made by performing more precise experiments.

### FUTURE PROBLEMS

The next steps to thermodynamic characterization of the Y123 superconductor are the investigation of this solid solution ordering, and modelling of liquid solutions in the system Y-Ba-Cu-O. Sets of self-consistent data for these two materials would permit us to predict by means of thermodynamic calculations the crystallization of phases from melts as well as the proper formation of ordered superconducting compounds.

### CONCLUSIONS

The phenomenological model of the Y123 phase considered here (2,3) correctly reflects its thermodynamic properties, and enables one to describe the experimental data with satisfactory accuracy.

To best fit the values of the model parameters all available thermodynamic and structural data on the Y123 phase have been combined in an optimization analysis. The description obtained in this way is directly amenable to computer treatment and automatic data retrieval, and at present it is unnecessary to derive for these purposes any new models or equations.

The system of the self-consistent thermodynamic data, presented by the model (2,3) and the values of the parameters in Table 3, unifies all current information on the thermodynamics of the Y123 solid solution obtained in 240 experiments. Thus, in the future the recommended description of this material can only be revised when new investigations of higher precision become available, or if new behavior of the Y123 phase is found (such as existence of the tetragonal-orthorhombic transformation under pressure or the possibility of oxygen indexes  $z$  being greater than 1). The detection of such new effects, however, will go hand in hand with more precision of the experimental observations. Figure 3 illustrates the benefit of the thermodynamic characterization of the Y123 phase recommended here. It shows an adequate description of the data on the precise experimental measurement of  $z(T)$  [92], which were not used for the assessment of the parameters in (2).

### ACKNOWLEDGMENTS

Comments and contributions made by the following persons during the compilation of this document are gratefully acknowledged: C. Chatillon, V. Kuzmenko, W. Metanowski, R. Metselaar, I. Mills, E. Rudnyi, H. Verweij.

### LIST OF ACRONYMS

|     |                                      |
|-----|--------------------------------------|
| ACL | adiabatic calorimetry                |
| CHA | chemical analysis of the composition |
| DSC | differential scanning calorimetry    |
| EMF | electromotive forces method          |
| MPM | manometers pressure measurement      |
| NDA | neutron diffraction analysis         |
| RES | resistance measurements              |
| SCL | solution calorimetry                 |
| TGA | thermal gravimetric analysis         |
| VLA | volumetric analysis                  |
| WLS | weighted least squares method        |
| XRD | X-ray diffraction                    |

### REFERENCES

1. M. K. Wu, J. R. Ashburn, C. J. Tong, R. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, C.W. Chu. *Phys. Lett.* **58**, 908 (1987).
2. G. F. Voronin and S.A. Degterov. *Physica C* **176**, 387 (1991).
3. H. Murakami, T. Suga, T. Noda, Y. Shiohara, S. Tanaka. *Jpn. J. Appl. Phys.* **29**, 2720 (1990).
4. A. J. Khachatryan, S. V. Semenovskaya, J. W. Morris. *Phys. Rev.* **37**, 2243 (1988).
5. J. F. Marucco, C. Noguera, P. Garoche, G. Collin, *J. Mater. Res.* **2**, 757 (1987).
6. A. Boudene, K. Hack, A. Mohammad, D. Neuschutz, E. Zimmermann, G. Effenberg, S. Fires, H.-L. Lukas, R. A. Konetzki, R. Schmid-Fetzer, W. Huang, B. Sundman, C. Bernard, C. Colinet, A. Pasturel, A. Pisch, F. Weiss, A. Rais, M. Ganteaume, J. C. Mathieu, J. Rogez, B. B. Argent, A.T. Dinsdale, A. Watson. *High Temp. Mater. Sci.* **35**, 159 (1996).

7. J. Plewa, H. Altenburg, J. Hauck. *Z. Metallkunde* **84**, 652 (1993).
8. E. B. Rudnyi, V. V. Kuzmenko, G. F. Voronin. *J. Phys. Chem. Ref. Data* **27**, 855 (1998).
9. S. A. Degtyarev. *Sverkhprovodimost: Fiz., Khim., Tech.* **3**, 115 (1990).
10. S. A. Degtyarev. *Sverkhprovodimost: Fiz., Khim., Tech.* **3**, 130 (1990).
11. I. A. Merzhanov and S. A. Degtyarev. *ibid.* **3**, 125 (1990).
12. V. V. Kuzmenko, E. B. Rudnyi, G. F. Voronin. *Zh. Fiz. Khim.* **74**, 227 (2000); English translation in *Russ. J. Phys. Chem.* **74**, 168 (2000).
13. G. F. Voronin, S. A. Degtyarev, Yu. Ya. Skolis. *Dokl. Akad. Nauk SSSR* **319**, 899 (1991); English translation in *Dokl. Phys. Chem.* **319**, 565 (1991).
14. P. Meuffels, B. Rupp, E. Porschke. *Physica C* **156**, 441 (1988).
15. P. Meuffels, R. Naeven, H. Wenzl, *ibid.* **161**, 539 (1989).
16. J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, M. S. Kleefisch. *Phys. Rev. B* **36**, 3608 (1987).
17. K. Ikeda, M. Nagata, M. Ishihara, S. Kumazawa, T. Shibayama, A. Imagawa, T. Sugamata, H. Katoh, N. Momozawa, K. Umezawa, K. Ihida. *Jpn. J. Appl. Phys.* **27**, L202 (1988).
18. H. Verweij and W. H. M. Bruggink. *J. Phys. Chem. Solids* **50**, 75 (1989).
19. I. V. Tarasov, V. N. Gus'kov, V. B. Lazarev. *Neorg. Mater.* **30**, 1588 (1994).
20. P. Gerdanian, C. Picard, J. F. Marucco. *Physica C* **157**, 180 (1989).
21. M. E. Parks, A. Navrotsky, K. Mocala, E. Takayama-Muromachi, A. Jacobson, P. K. Davies. *J. Solid State Chem.* **79**, 53 (1989).
22. G. F. Voronin and S. A. Degtyarev. *Zh. Fiz. Khim.* **67**, 1351 (1993); English translation in *Russ. J. Phys. Chem.* **67**, 1213 (1993).
23. T. Matsui, T. Fujita, K. Naito, T. Takeshita. *J. Solid State Chem.* **88**, 579 (1990).
24. G. A. Sharpataya, Z. P. Ozerova, I. A. Konovalova, V. B. Lasarev, I. S. Shaplygin. *Neorg. Mater.* **27**, 1674 (1991).
25. A. S. Monaenkova, A. A. Popova, N. V. Zaitseva. *Zh. Fiz. Khim.* **69**, 1543 (1995).
26. A. M. Azad and O. M. Sreedharan. *Supercond. Sci. Technol.* **3**, 159 (1990).
27. Z. Fan, C. J. Ji, Z. Zhao. *J. Less-Common Met.* **161**, 49 (1990).
28. Yu. Ya. Skolis, S. F. Pashin, S. V. Kitsenko, M. L. Kovba, D. V. Fomichev. *Tezisy dokladov 13 Vsesoyuznoi konferentsii po khimicheskoi termodinamiki i kalorimetrii, Krasnoyarsk, V. 1*, p. 62 (1991).
29. S. J. Burns. *Supercond. Sci. Technol.* **7**, 337 (1994).
30. E. D. Specht, C. J. Sparks, A. G. Dhere, J. Brynstad, O. B. Cavin, D. M. Kroeger, H. A. Oye. *Phys. Rev. B* **37**, 7426 (1988).
31. B. Touzelin and J. F. Marucco. *J. Less-Common Metals.* **144**, 283 (1988).
32. H. M. O'Bryan and P. K. Gallagher. *Solid State Ionics.* **32/33**, 1143 (1989).
33. S. G. Titova, S. G. Sludnov, V. F. Balakirev, O. M. Fyodorova, T. I. Arbutova, O. V. Morozova. *Ceram. Int.* **22**, 471 (1996).
34. J. Mizusaki, H. Tagawa, K. Hayakawa, K. Hirano. *J. Am. Ceram. Soc.* **78**, 1781 (1995).
35. R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, D. Werder. *Nature* **329**, 432 (1987).
36. N. V. Jaya, S. Natarajan, S. Natarajan, G. V. Subba Rao. *Solid State Commun.* **67**, 51 (1988).
37. W. H. Fietz, M. R. Dietrich, J. Ecke. *Condens. Matter.* **69**, 17 (1987).
38. I. V. Alexandrov, A. F. Goncharov, C. M. Stishov. *Pisma v JETF (Rus. J. of Theor. and Experim. Phys.)* **47**, 357 (1988).

39. K. Suenaga and G. Oomi. *J. Phys. Soc. Jap.* **60**, 1189 (1991).
40. K. Suenaga, K. Nishinura, T. Kagayama, G. Oomi. *Phys B* **199&200**, 262 (1994).
41. M. Cankurtaran, G. A. Saunders, J. R. Willis, A. Al-Kheffaji, D. R. Almond. *Phys. Rev. B* **39**, 2872 (1989).
42. E. B. Rudnyi. *Chemometrics Intel. Lab. Systems* **34**, 41 (1996).
43. E. B. Rudnyi. *Chemometrics Intel. Lab. Systems* **36**, 213 (1997).
44. C. R. Rao, J. Kleffe. *Estimation of Variance Components and Applications*, North-Holland Series in Statistics and Probability, V.3, North-Holland, Amsterdam (1988).
45. G. F. Voronin. *Materials and Crystallographic Aspects of  $HT_c$ -Superconductivity*, E. Kaldis (Ed.), NATO ASI Series, Series E, V. **263**, Kluwer Academic Publ., Dordrecht/Boston/ London (1994).
46. H. M. O'Bryan and P. K. Gallagher. *Adv. Ceram. Mater.* **2**, 640 (1987).
47. M. O. Eatough, D. S. Ginley, B. Morosin, E. L. Venturini. *Appl. Phys. Lett.* **51**, 367 (1987).
48. A. T. Fiory, M. Gurvitch, R. J. Cava, G. P. Espinosa. *Phys. Rev. B* **36**, 7262 (1987).
49. I. K. Schuller, D. C. Hinks, M. A. Beno, D. W. Capone-II, L. Soderholm, J. P. Locquet, Y. Bruynseraede, C. U. Serge, K. Zhang. *Solid State Commun.* **63**, 385 (1987).
50. Y. Kubo, Y. Nakabayashi, J. Tabuhi, T. Yoshitake, A. Ochi, K. Utsumi, H. Igarashi, M. Yonezawa. *Jpn. J. Appl. Phys., Part 2*, **26**, L1888 (1987).
51. K. Yukino, T. Sato, S. Ooba, M. Ohta, F. P. Okamura, A. Ono. *Jpn. J. Appl. Phys.* **26**, L869 (1987).
52. E. Takayama-Muromachi, Y. Uchida, K. Yukino, T. Tanaka, K. Kato. *Jpn. J. Appl. Phys.* **26**, L665 (1987).
53. M. Kogachi, S. Nakanishi, K. Nakahigashi, S. Minamigawa, H. Sasakura, N. Fukuoka. *Jpn. J. Appl. Phys.* **27**, L1228 (1988).
54. H. Wang, D. X. Li, W. J. Thomson. *J. Am. Ceram. Soc.* **71**, C463 (1988).
55. P. Strobel, J. J. Capponi, M. Marezio, P. Monod. *Solid State Commun.* **64**, 513 (1987).
56. S. Yamaguchi, K. Terabe, A. Saito, S. Yahagi, Y. Iguchi. *Jpn. J. Appl. Phys., Part 2*, **27**, L179 (1988).
57. K. Fueki, Y. Idemoto, H. Ishizuka. *Physica C* **166**, 261 (1990).
58. J. S. Kim and D. R. Gaskell. *J. Am. Ceram. Soc.* **77**, 753 (1994).
59. T. B. Lindemer, J. F. Hunley, J. E. Gates, A. L. Sutton, J. Brynstad, P. K. Gallagher. *J. Am. Ceram. Soc.* **72**, 1775 (1989).
60. K. Conder, J. Karpinski, E. Kaldis, S. Rusiecki, E. Jilek. *Physica C* **196**, 164 (1992).
61. E. Salomons, N. Koeman, R. Brouer, D. G. de Groote, R. Griessen. *Solid State Commun.* **64**, 1141 (1987).
62. R. Bormann and J. Nolting. *Appl. Phys. Lett.* **54**, 2148 (1989).
63. K. Kishio, J. Shimoyama, T. Hasegawa, K. Kitazawa, K. Fueki. *Jpn. J. Appl. Phys.* **26**, L1228 (1987).
64. M. Tetenbaum, B. Tani, B. Czech, M. Blander. *Physica C* **158**, 377 (1989).
65. P. Schleger, W. N. Hardy, B. X. Yang. *ibid.* **176**, 261 (1991).
66. T. Mathews and K. T. Jacob. *Metall. Trans. A* **23A**, 3325 (1992).
67. E. L. Brosha, F. H. Garson, I. D. Raistrick, P. K. Davies. *J. Am. Ceram. Soc.* **78**, 1745 (1995).
68. B. J. Lee and D. N. Lee. *J. Am. Ceram. Soc.* **74**, 78 (1991).
69. V. S. Grunin, M. M. Pivovarov, I. B. Patrina, M. V. Razumeenko, R. A. Bubnova, M. I. Domnina, M. M. Shul'ts. *Dokl. Akad. Nauk SSSR* **307**, 143 (1989).
70. F. H. Garzon, I. D. Raistrick, D. S. Ginley, J. W. Halloran. *J. Mater. Res.* **6**, 885 (1991).

71. J. H. Choy, S. G. Kang, Q. W. Choi, D. Y. Jung, G. Demazeau. *Mater. Lett.* **15**, 156 (1992).
72. Y. Idemoto, J. Takahashi, K. Fueki. *Physica C* **194**, 177 (1992).
73. V. V. Prisedskii, O. V. Zinchenko, E. V. Lotar, V. V. Klimov. *Dokl. Akad. Nauk Ukr.* **4**, 130 (1993).
74. L. R. Morss, D. C. Sonnenberger, R. J. Thorn. *Inorg. Chem.* **27**, 2106 (1988).
75. A. S. Monaenkova, A. A. Popova, N. V. Zaitseva, M. A. Bykov, M. L. Kovba. *Zh. Fiz. Khim.* **68**, 603 (1994).
76. N. I. Matskevich, T. L. Popova, V. A. Titov, B. S. Kravchenko, B. P. Shaburova, O. G. Potapova. *Zh. Fiz. Khim.* **67**, 1342 (1993).
77. Z. G. Zhou and A. Navrotsky. *J. Mater. Res.* **7**, 2920 (1992).
78. Z. Hengzhong, F. Zheng, Z. Pingmin, C. Xinmin. *J. Solution Chem.* **24**, 565 (1995).
79. G. F. Voronin and I. A. Uspenskaya. *Zh. Fiz. Khim.* **71**, 1750 (1997); English translation in *Russ. J. Phys. Chem.* **71**, 1572 (1997).
80. G. F. Voronin. *Pure Appl. Chem.* **64**, 27 (1992).
81. D. E. Morris, N. G. Nickel, R. L. Sid, J. Y. T. Wei. *Physica C* **159**, 287 (1989).
82. R. Beyers and B. T. Ahn. *Ann. Rev. Mater.* **21**, 335 (1991).
83. J. L. MacManus-Driscoll. *Adv. Mater.* **9**, 457 (1997).
84. P. Karen and A. Kjekshus, *J. Therm. Anal.* **48**, 1143 (1997).
85. K. S. Gavrichev, V. E. Gorbunov, I. A. Konovalova, V. B. Lasarev, E. A. Tishchenko, I. S. Shaplygin. *Izv. AN SSSR, Neorg. Mater.* **24**, 343 (1988).
86. A. Junod, D. Eckert, G. Triscone, V. Y. Lee, J. Muller. *Physica C* **159**, 215 (1989).
87. R. Shaviv, E. F. Westrum, R. J. C. Brown, M. Sayer, X. Yu, R. D. Weir. *J. Chem. Phys.* **92**, 6794 (1990).
88. T. Atake, A. Honda, H. Kawaji. *Physica C* **190**, 70 (1991).
89. M. S. Sheiman, S. A. Churin, G. P. Kamedova, G. K. Shvetsova, P. I. Nikolaev. *Tezisy dokladov XII Vsesoyuznoi konferentsii po khimicheskoi termodinamike i kalorimetrii, Gorkii*, V. **1**, P. 140 (1988).
90. C. Picard and P. Gerdanian. *J. Mater. Chem.* **6**, 619 (1996).
91. S. Yang, H. Claus, B. W. Veal, R. Wheeler, A. P. Paulikas, J. W. Downey. *Physica C* **193**, 243 (1992).
92. H. Verweij, W. H. M. Bruggink, R. A. Steeman, E. Frikkee, R. B. Helmholtz. *Physica C* **166**, 372 (1990).