ON THE CHRONICLE OF HIGH-T_c OXIDE SUPERCONDUCTORS
Interdisciplinary of thermochemistry, stoichiometry and thermodynamics

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Abstract

After briefly noting some development records in phase diagrams, the stoichiometry is dealt with in more details showing the structural layer ordering in the superconducting cuprates and mentioning some correlation between thermodynamics and BSC theory of superconductivity.

Keywords: cuprates, stoichiometry, superconductivity, thermodynamics

Introduction

In the 1990s the thermochemical research was the main engine in the boom progress of new sort of superconducting materials called the high T_c superconductors (HTSC). Specialized thermoananlytical studies at low temperatures became a useful tool in depicting characteristic behavior. The crucial impulse was the surprising discovery that a ceramic sample, i.e., barium-doped lanthanum copper oxides become superconducting at 36 K, some 12 K above the previous record temperature for traditional transition metals alloys. The subsequent quest for the other promising cuprates yielded materials with transition temperature (T_c) far above the boiling temperature of nitrogen (77 K) so that they could be used with cheaply available coolant rather than expensive liquid helium. Although the research boom is gradually expiring the commercial applications have been too slow to take off and the early promise of magnetically-levitated trains, powerful electric motors or super-efficient power transmission has not been met.

A major difficulty with the ceramic HTSC is that such complex metal oxides have high mechanical fragility so its ability to bend is severely limited. Although this has been overcome by surrounding its filaments with the highly pliable metals (Ag) there is also a ceiling on the amount of current that can be carried and another level of magnetic field in which the system can be operated. Other effort to bond cuprate superconductors to substrates has a target: melt and liquid coating methods, in the hope

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to cut the cost. Most progressive seems to be the growth of buffer layer directly onto a Ni-alloy where intermediate NiO layer exhibits good compatibility with HTSC. Such a liquid phase epitaxy (LPE), with no need of high-vacuum components, is cheaper to build as compared with traditional chemical vapor deposition (CVD) and provides higher growth rates. Electrical engineers are looking forward to some of such processes that can help reducing the capital and operating costs of using HTSC. For example, unlike conventional large copper wire-based power transformers, which are cooled by oil and have to be located outside on hard standings massive enough to support their weight, HTSC equivalents would use liquid nitrogen, which is widely available commodity, cheap enough and intrinsically secure making available much lighter units so that they could be installed indoor safely, near to the point of power use. The process of entire HTSC applicability seems to replicate another case of metallic glasses, equally innovative and promising material of seventies, that never get actually in practical use in transformers due to unanswered intricacy of their thermodynamic stability. In that case thermochemical research contributed most influential function, too. Nevertheless there is the first important HTSC application, worth mentioning, as a security switch in high power electric circuits, where the massive rod of HTSC is coupled in-between and kept near the critical current state to secure short-cut's explosions that often happen when using classical fusses.

We are happy to mention that in our mother Institute of Physics we took early part in the worldwide development of HTSC having been interested in various aspects of structural and preparative thermochemistry, thermodynamics and even technology of phases as well as, more recently, in certain theoretical aspects of superconductivity. Among others the investigations near the beginning were: the characterization of famous phase, YBa$_2$Cu$_3$O$_x$, abbreviated as (111) [1], initial studies in quenched (111) [2] (which we, unfortunately, did not completed to develop practical utilization for HTSC wire texturing while drowned by means of fast melt solidification and glass-pattern recrystallization [3–5]), early description of kinetic problems with the (111) phase formation and decomposition [6], etc., not mentioning the growth of single crystals and various methods of powder technologies.

It is clear that thermochemical research played a decisive role so that it became also reflected in extended publication activity in relevant journals, namely J. Thermal Analysis and Thermochimica Acta and herewith published special issues [7, 8]. The progress of HTSC has been always associated with better understanding of phases and phase diagrams starting from the oxide (Cu, Ba, Y), their binaries [9, 10] through pseudobinaries up to the Y–Ba–Cu–O pseudoternaries [9–14]. We paid increased attention to the improvement of calculation of phases and their thermodynamic data [15, 16], the construction of phase diagrams, which also proceeded with the novel families of Bi–Ca–Sr–Cu–O [17, 18] and Hg–Ca–Ba–Cu–O [19, 20] systems. More than ten years experience with the construction of various types of phase diagrams and investigation procedures (to estimate associated thermodynamic data) were summarized in our previous reports [12–14, 21, 22]. We put in use a specific representation depicting the behavior of volatile phases (O$_2$, Hg) enabling construction of so-called chemical potential diagrams in two- and three-metal system, portrayed in Fig. 1 [23].
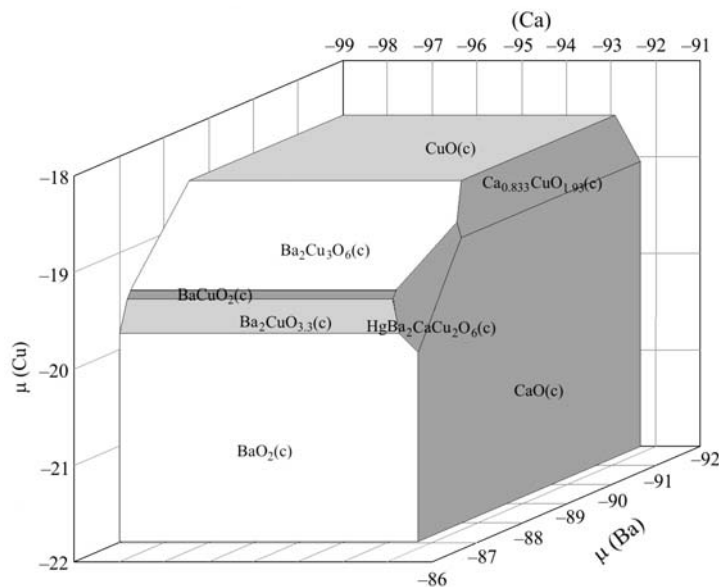
Fig. 1 Account on plausible phases and their stoichiometry to occur in the system Ba–Ca–Cu–Hg–O. It is illustrated by the three-dimensional plot of chemical potential (μ) for three metals involved (Ba–Ca–Cu) in the conservative stage (c) assuming two volatile components (O and Hg) at the temperature T=773 K and pressure P=1 atm. The re-reproduced computer print-out was provided by the courtesy of Prof. H. Yokakawa (Tsukuba, Japan)

In contradiction to the structural models we could hypothetically account just for the stoichiometric existence of various phases yet unknown by a formal extending the cation ratios to ranges of yet undetermined compounds but suitable for thermodynamic calculations. Such hypothetical changes of ratios (Y+Ba)/Cu (from <1, through ≈2 to >2.5) can be derived, on one side, from the basic superconductor $YBa_2Cu_3O_x$, and on the other side, from the non-superconducting 'green phase' Y_2BaCuO_x (211). We can also extract partial values for the formation enthalpy along such homological series. For example, according to the stoichiometry changes along

$$YBa_2Cu_3O_7 \rightarrow YBa_2Cu_4O_8 \rightarrow YBa_2Cu_5O_9 \rightarrow (1/2)Y_2Ba_4Cu_7O_{15}$$

we can estimate that each adding of a single CuO conveys 19.8 kJ mol^{-1}, while that for Cu_2O is 12.13 kJ mol^{-1} and the multiplication of BaO layers provides the value between 29–32 kJ mol^{-1} [12].

By using a particular thermoanalytical technique a special feature of the HTSC behavior was elucidated, such the emanation thermal analysis in determining oxygen changes in Ba-cuprates [6, 24] or sorptometric measurements aimed to analyze the surface heterogeneity of Hg-cuprates showing its fractal-like dimensions [25]. In this report, however, we want to concentrate to HTSC as viewed from yet another cross-disciplinary aspects of thermochemistry, thermodynamics and thermal physics as a matter of interest for some involved thermoanalysts.

Stoichiometry and superconducting state

Superconductivity, one of the most fascinating phenomena in solid-state physics was discovered in 1911 by Kamerlingh Onnes [26] but it was until 1957 that a satisfactory microscopic theory of the effect became available, i.e., one by Bardeen, Cooper and Schieffer (BBC) [27]. The special correlation responsible for superconductivity are pair correlations, which in the presence of electron attraction leads to the formation of electron pairs, often called Cooper pairs [28]. Each pair can be considered as a bound state of two electrons with opposite spin and momentum and may form even if the interactions are repulsive due to certain stringent requirements (i.e., the interactions must be much less repulsive for electrons near the Fermi surface than away from it and electron pairs can be treated as being independent of each other).

Impurity atoms in a material are usually viewed as a problem because they can result in properties deviating from those ideally assumed. However, they can be sometimes used to advantage when attempting to understand new complex materials. This is because the interaction of such doping atoms with matrix can reveal detailed information on the local electronic environment, which is the case of HTSC. Here the electron–electron attractive interactions occur in the degenerated electron gas as a result of the formation of above-mentioned Cooper-pairs. The superconducting ground-state represents 'condensation' of these Cooper-pairs into a single macroscopic quantum state – a process analogous to the fundamental Bose–Einstein condensation. The order parameter associated with this ground-state has d-wave symmetry. The examples of the HTSC materials are shown in Table 1. Whereas in these systems the conduction is due to holes in the another, electron-doped system of $Nd_{2-x}Ce_xCuO_4$ ($T_c \cong 20$ K) this is different.

The common structural features of all HTSC is a perovskite network $MMeO_3$ [29] formed by densely coordinated oxygens being the source of two sublattices, one with the large M ($\equiv$Ba, Sr) cations with 12-coordination and small Me ($\equiv$Cu) cations with 6-coordination. The most important structural element are the copperoxide planes with a unit cell CuO_2, which are formed from octahedral, pyramids or squares. Examples are $La_{2-x}Sr_xCuO_4$, where the planes are formed from octahedral, $YBa_2Cu_3O_7$ from pyramids and $Nd_{2-x}Ce_xCuO_4$ from squares. The electron transport and the physical processes leading to superconductivity are believed to take place within these planes. In the simplest case of $LaCuO_4$ the CuO_6 octahedra are elongated due to the Jahn–Teller distortion, lifting the degeneracy of the Cu–d orbitals, which is two- and three-fold. This leaves for Cu a valency 2+ implying a $3d^9$ configuration. The hole in the $3d$ shell is placed into the highest anti-bonding Cu–O state, which has predominantly $3d_{x2-y2}$ character. With one hole per formula unit of $LaCuO_4$, one can expect its metallic character with a half-filled conduction band. La_2CuO_4 can be doped with holes by partial replacing La^{3+} by Sr^{2+}, similarly Nd_2CuO_4 can be doped with electrons by the replacement of Nd^{3+} with $Ce^{3.5+}$. The Cu–O planes of $YBa_2Cu_3O_7$ contains holes without further modification because the charge is moved from the planes into the chains (so-called self-doping), which are formed from CuO_4 squares sharing an oxygen atom.

Table 1 Structural layer ordering in the superconducting cuprates and their critical temperatures for n=1, 2, 3 and 4

| Superconducting cuprates	Critical temperature/K for			
	n=1	n=2	n=3	n=4
Y-cuprates	93	80	–	–
$YBa_2Cu_{2+n}O_{5+n+\delta}$				
$\Downarrow \delta$	$\Uparrow e^-$			
$[CuO_\delta]^{2(1-\delta)+}\,[BaO]^0\,[CuO_2]^{2-}\,[Y]^{3+}$	$[CuO]^{2-}\,[BaO]^0\,[CuO]^{2(1-\delta)+}$			
Bi-cuprates	12	85	108	–
$Bi_2Sr_2Ca_{n-1}Cu_nO_{2n+4+\delta}$				
$\Downarrow \delta$	$\Uparrow e^-$			
$[BiO]^+\,[BiO]^+\,[SrO]^0\,[CuO_2]^{2-}\,[Ca]^{2+}$	$[CuO_2]^{2-}\,[SrO]^0\,[BiO]^+\,[BiO]^+$			
Tl-cuprates	95	118	125	–
$Tl_2Ba_2Ca_{n-1}Cu_nO_{2n+4+\delta}$				
$\Uparrow Tl$	$\Uparrow e^-$			
$[TlO]^+\,[TlO]^+\,[BaO]^0\,[CuO_2]^{2-}\,[Ca]^{2+}$	$[CuO_2]^{2-}\,[BaO]^0\,[TlO]^+\,[TlO]^+$			
$TlBa_2Ca_{n-1}Cu_nO_{2n+3+\delta}$				
$\Uparrow \delta$	$\Downarrow e^-$			
$[TlO]^+\,[BaO]^0\,[CuO_2]^{1.66-}\,[Ca]^{2+}$	$[CuO_2]^{1.66-}\,[BaO]^0\,[TlO]^+$			
Hg-cuprates	98	120	135	118
$Hg_2Ba_2Ca_{n-1}Cu_nO_{2n+2+\delta}$				
$\Downarrow \delta$	$\Uparrow e^-$			
$[HgO_\delta]^{(2-2\delta)+}\,[BaO]^0\,[CuO_2]^{2-}\,[Ca]^{2+}$	$[CuO_2]^{2-}\,[BaO]^0\,[HgO_\delta]^{(2-2\delta)+}$			

Among the most suitable cuprates are those fulfilling relation, $d_{M-O} \leq \sqrt{2}d_{Me-O}$ and containing one (or preferably more) crystal planes per unit cell that are consisting of only Cu and O atoms in a planar square lattice, cf. Table 1. In order to keep electroneutrality the MeO must be strictly 2+, which determine the choice of M-cation. The cations with the formal charge 4+ exhibit only small ionic radius and thus can bear an insufficient number of neighboring oxygens. The solution grant access to structures either with deficiency of anions ($YBa_2Cu_3O_x$) or exhibiting more combine constitution (Tl, Hg-based structures). The basic configuration reveals three parallel layers, $[CuO_2][MO][M'O]$, necessarily associated with overlapping of electron orbitals ($Cu - 3d_{x2-z2}$ and $O - 2p_{x,z}$). As mentioned, superconductivity originates from the strongly interacting electrons in these CuO_2 planes (Cu atoms are believed to be in the $Cu^{2+} - 3d^9$ configuration with the spin ½ so that the overall electronic state is the antiferromagnetic Mott insulator). Doping these insulating CuO_2 layers with holes (or electrons) causes the appearance of new electronically ordered state which includes that of superconductivity because the mutual hopping of electrons from Cu to Cu becomes possible. A generally known schematic phase

diagram of such cuprates reveals 'optimum' hole-doping near the hole concentration about 0.2 per Cu atom (with inter-atomic distance of about 0.3 nm, the Fermi wavelength of about 1 nm and superconducting coherence length of about 1.5 nm).

Important role plays the complex 'ceramic' morphology of these materials. Most HTSC are composed of grains (expectantly to be oriented along the current) the interface of which is responsible for the composition adjustments by enabling desirable easy-interaction with surrounding oxygen. Therefore we can expect intimate relation between HTSC properties and the material morphology depending on the way of foregoing technological treatment. We try to avoid the formation of insulating layers, the contamination by reactive gases (CO_2, H_2O) or the incorporation of impurities from the sample holders or precursors, although, some impurities may turn out agreeable when serving as pinning centers (such as unreacted Y_2O_3 itself) for super-current vortexes.

Although we use to take care about off-stoichiometry and second phases occurrence in bulk we have to be also careful about the composition peculiarities on the interfaces where high curvature of the $YBa_2Cu_3O_x$ crystallites may even change the local oxygen stoichiometry, x, by depletion of oxygen on surface stress sites with the consequent formation of week links, Fig. 2a. Tentatively, it may result in the drift of the low-temperature curve tails experimentally measured on the plot of relative conductivity *vs.* temperature. Similar consequence was early studied by the electric field effect resulting in the field-driven oxygen rearrangement [30] arising from the field-driven movement of the mobile charge carriers in HTSC being thus a generic property of these superconductors.

Another awkward effect can be found in the HTSC vicinity layer of super-current channels where cation stoichiometry may not stay stable but its intimate links
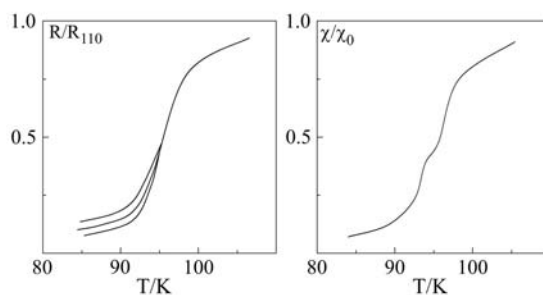
Fig. 2 a – Schematic plot of relative electric resistivity, R_r, *vs.* temperature, T, showing the effect of higher surface energy on stress sites along the highly-curved interfaces. It may induce rather negligible changes in the surface oxygen stoichiometry but, nevertheless, it may remain effective enough to modify the course of the tailing curve descending after the inflection point to minimum resistivity at low temperatures. b – Schematic plot of thermal dependence of magnetic susceptibility, χ, at low temperatures, T, may well testify its stepwise change as the curve exhibits the ascension of superconductivity due to the gradual inter-linking of individual structural blocks at different levels of their efficacy at flat (chains, areas) and space (sector) compass

can be strongly modified [21]. The real (111) composition, with the oxygen content at $x = 6.85$, can contain both the two- and trivalent cations of copper as well as holes ($\square$) such as $YBa_2Cu_{2.6}Cu_{0.4}\square_{0.15}O_{6.85}$. Under the effect of negative-charge of super-current flow on the very thin neighboring layers it may induce not only the phase structure deformation but also certain chemical changes due to the possible absorption of some species, likely Ba^{2+} and $\square^{2+}$, that can migrate from the internal body of HTSC. The intact interface composition can then carry through a curiously wide range of stoichiometry, e.g.,

$$YBa_{3.03–3.09}Cu_{0.392–0.26}Cu_{0.4}\square_{0.223–0.226}O_{5.744–5.677}$$

as theoretically shown in [21].

Yet another source of curiosity may be established when making SQUID measurements on the $YBa_2Cu_3O_x$ single crystals [31] where we can witness stepwise sequences of gradual transfer of dimensionality, D, from the 2-D to 3-D superconducting state, Fig. 2b. Although first indication of superconductivity turns up to be as high as 92 K the internal dissipation processes hold back its instantaneous progress down to 85 K. It is because the $[CuO_2]^{2–}$ layers turn more easily to the superconducting state on cooling (already at $T_1=91.2$ K) while at 2 K lower the same is done by whole blocks of ($[CuO_2]^{2–}$ $[Y]^{3+}$ $[CuO]^2$) until the whole-bulk superconductivity is achieved at yet 4 K lower via tunneling Ba–CuO–Ba barriers. It, however, does not comply with the classical BCS theory but it seems to be more correlative to the antiferromagnetic arrangement in 2-dimensional systems.

Thermodynamics and BCS theory

Onset of superconductivity bears special features because all linear dc transport coefficients disappear. Material parameters are thus deduced rather from equilibrium properties, would they be of the thermodynamic nature or from the spectral measurements. Apparently the HTCS escape the traditional BCS [27] theory including its generalization by Eliashberg to strongly coupled superconductors [29]. The critical temperature is nearly by an order of magnitude larger than it is common for the conventional superconductors of a comparable electronic density of states. Moreover, the critical values of temperature, T_c, magnetic field, H_c, and magnetostriction, dV/dH, the thermal capacity, c_p, the discontinuity of c_p at the critical point, and the energy gap are not interrelated by ratios found in conventional superconductors. This fact immediately boosted a search for a new mechanism of the superconductivity.

While in the study of conventional superconductors the major headway was made possible by physical measurements (discovery of the superconductivity itself, the Meissner effect, the isotop effect, the energy gap seen first in the specific heat and later in the tunneling, and so on), in the case of HTSC the most important test of new theories provided a large variety of materials in which the CuO_2 planes are embedded in quite different ionic backgrounds. Chain-free materials soon ruled out the very first theories based on the superconductivity of CuO chains, only. Similarly, materials in which the assumed ingredient is missing eliminated the ionization of the apical oxy-

gen, the orthorhombic distortion, the breezing phonon mode, and other coupling mechanisms. For theories based on the dominant role of CuO_2 planes the crucial test was the sensitivity of the critical temperature to the substitution of electronically neighboring zinc into Cu(2) positions.

The physical measurements turned in a great part towards magnetic properties of the HTSC. In the conventional isotropic superconductors the magnetic field is either expelled or is forming the Abrikosov vortex lattice. The THSC materials are, in general, highly anisotropic with the anisotropy ratio ranging from moderate values leading to the anisotropic three-dimensional behavior to large values showing clear two-dimensional features. These regimes make possible to achieve new phases of the vortex matter would they be the vortex liquid, braking of vortices into pancakes, or the system mutually orthogonal Josephson and Abrikosov vortices [29] penetrating each other in two-dimensional-like systems. Though rearrangements of the vortex matter correspond to rather small changes of the free energy, these transitions are detectable by the specific heat. Such thermodynamic measurements together with magnetic measurements, neutron diffraction and direct observation of the structure via vortex decoration provide the experimental background for the vortex matter comparable to the early studies of phase transitions in solids. The theory has followed this step from back into the history as the interest has shifted from the microscopic treatment towards the phenomenological approach of Ginzburg–Landau type. Some advanced calculation [32] were done in studying the electrostatic potential in a superconductor applying the Maxwell equation for the vector potential, the Schroediger equation for the wave function and the Poisson equation for the electrostatic potential. It follows that the electrostatic and the thermodynamic potential compensate each other to a great extent resulting into an effective potential acting on the superconducting condensate.

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References

1 M. Nevřiva, E. Pollert, J. Šesták and L. Matějková, Thermochim. Acta, 136 (1988) 263; Physica C 153/155 (1988) 377.
2 J. Šesták M. Nevřiva, E. Pollert and J. Hejtmanek, Thermochim. Acta, 132 (1988) 35.
3 Z. Strnad and J. Šesták, Thermochim. Acta, 174 (1991) 253.
4 J. Šesták in A. V. Narlicar, Ed. 'Studies of HTSC', Nova Sci. Publ., New York 1991, 7, p. 23.
5 K. Salama and D. F. Lee, Supercon. Sci. Tech., 7 (1994) 193.
6 J. Šesták and N. Koga, Thermochim. Acta, 203 (1992) 321.

 7 'Oxide high T_c superconductors' Eds P. Gallagher, T. Ozawa and J. Šesták, Thermochim. Acta, 174, Elsevier 1991.

 8 'High temperature superconductors' Ed. M. Leskelä, J. Thermal Anal., 48, Wiley 1997.

 9 R. S. Roth in M. F. Yen, Ed., Ceramic Superconductors, Amer. Cer. Soc. Inc., Westerville 1988, Vol. II, p. 13.

10 J. Šesták, Pure Appl. Chem., 64 (1992) 125.

11 N. Ilynych, S. Zaitseva, G. Moiseev, J. Šesták and N. Vatolin, Thermochim. Acta, 266 (1995) 285.

12 J. Šesták, D. Sedmidubsky and G. Moiseev, J. Therm. Anal. Cal., 48 (1997) 1105.

13 P. Karen and A. Kjekhus, J. Therm. Anal. Cal., 48 (1997) 1143.

14 G. Moiseev, N. Vatolin and J. Šesták, J. Mining Metal., Bor 33 (1997) 105.

15 J. Šesták, G. Moiseev and D. Tzagareishvili, Jpn. J. Appl. Phys., 33 (1994) 97.

16 G. Moiseev, N. Ziablikova, V. Jzukovski, N. Ilynych, S. Zaitseva and J. Šesták, Thermochim. Acta, 282/283 (1996) 191.

17 G. Moiseev, J. Šesták, N. Ilynych, S. Zaitseva and V. Vatolin, Netsu Sokutei Jap., J. Therm. Anal. Cal., 24 (1997) 158.

18 G. Moiseev, J. Šesták , V. Jzukovski, I. Garipova and S. Zaitseva, Thermochim. Acta, 318 (1998) 201.

19 D. Sedmidubský, J. Leitner, K. Knižek, A. Strejc and M. Veverka, Physica C., 329 (2000) 191.

20 D. Sedmidubský, J. Šesták, H. Yokakawa, A. Strejc and J. Lejtner, 'Phase diagrams in the Hg–Ba–Ca–Cu–O system', presented at the 12th ICTAC, Copenhagen 2002.

21 G. Moiseev, J. Šesták and B. Štěpánek, Ceramics/Silikaty, Prague 38 (1994) 143.

22 G. Moiseev and J. Šesták, Prog. Cryst. Growth Char., 30 (1995) 23.

23 H. Yokakawa, S. Yamuachi and T. Matsumoto, Thermochim. Acta, 245 (1994) 45.

24 V. Balek and J. Šesták, Thermochim. Acta, 133 (1988) 23.

25 P. Staszuk, D. Sternik and G. W. Chadzynski, J. Therm. Anal. Cal., 71 (2003) 173.

26 H. Kamerlingh Onnes, Akad. Wetenschappen, Amsterdam 14 (1911) 113.

27 J. Bardeen, L. N. Cooper and J. R. Schieffer, Phys. Rev., 108 (1957) 1175.

28 L. N. Cooper, Phys. Rev., 104 (1956) 1189.

29 N. M. Plakida 'High-temperature Superconductivity' Springer, Berlin 1995.

30 T. Frey, J. Mannhart, J. G. Bednorz and E. J. Williams, Phys. Rev., B51 (1995) 3257.

31 Z. Janu (Institute of Physics), private communication (1999).

32 P. Lipavsky, K. Morawetz and E. H. Brandt, Phys. Rev., B65 (2002) 65.