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(Received 9 October 1989)

ABSTRACT

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In a landslide of publications on high-T_c superconductors, the thermodynamic investigations play a modest role. Nevertheless, since thermodynamics is the physico-chemical basis of inorganic syntheses, we would like to draw the attention of materials science specialists to the results already published in this field and the ensuing possibilities, and also to stress that much still remains to be done on the thermodynamics of high-T_c compounds. This is the purpose of this review.

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The majority of measurements of the low-temperature heat capacity of oxide superconductors was made in connection with other investigations (electric, magnetic, etc.). The main purposes of $C_p(T)$ studies were the following:
(i) to obtain thermodynamic properties;
(ii) to ensure that the electrical conductivity and heat capacity leaps are concurrent;
(iii) to measure the absolute value of the ΔC_p leap and to calculate the superconductor parameters on this basis;
(iv) to look for some other anomalies of C_p;

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TABLE 1

Heat capacity, entropy and enthalpy of high-T_c superconductors at $T = 298.15$ K

Compound	$C_p^\ominus(T)$ ($\mathrm{J\ mol^{-1}\ K^{-1}}$)	$S^\ominus(T)$ ($\mathrm{J\ mol^{-1}\ K^{-1}}$)	$H^\ominus(T) - H^\ominus(0)$ ($\mathrm{J\ mol^{-1}}$)	Reference
La_2CuO_4	151.3	178.1	27750	11
$La_{1\ 8}Sr_{0.2}CuO_4$	152.4	179.7	27990	10
$YBa_2Cu_3O_{7-x}$	285.8	323.5	51230	12
	282.1	321.7	50790	13
$HoBa_2Cu_3O_{7-x}$	290.6	344.3	52620	14
	292.4	342.5	54850	13
$YbBa_2Cu_3O_{7-x}$	291.0	338.7	52270	13
$GdBa_2Cu_3O_{7-x}$	316.1	345.4	56040	15
$Bi_2Sr_2Ca_{1.2}Cu_{1.8}O_{8+\delta}$	346.7	406.7	62640	16
$Tl_{0\ 7}Ba_{2.1}Ca_2Cu_{3\ 3}O_{8+\delta}$	372.2	424.5	66320	17

low-T_c superconductors the electronic contribution is described by an exponential term. If the electronic contribution can be described by a linear function, then the electrons are in a normal rather than a superconducting state. This can be explained either by an alternative (not BCS) mechanism of superconductivity or by the high concentration of impurities having electrons in a normal state.

As for the high-temperature heat capacity, the $C_p(T)$ values for La_2CuO_4 in the temperature range 300–750 K measured by the DSC method have been reported only in ref. 18. In the region 240–640 K a diffused maximum was observed which is connected with a structural phase transition from the low-temperature orthorhombic to the high-temperature tetragonal modification (structural type K_2NiF_4 [1]). From the phase transition parameters ($\Delta H = 670$ J mol^{-1}; $\Delta S = 1.5$ J mol^{-1} K^{-1}), it can be expected that a gradual structural rearrangement would be observed in a wide temperature range and without noticeable changes in the lattice vibrations.

$LnBa_2Cu_3O_{7-x}$ compounds

These are known as 1 : 2 : 3 compounds. Preparation of the compounds is much more complicated than for $La_{2-x}M_xCuO_4$. It involves several heating–grinding cycles to increase the oxygen concentration, since it has been well established that samples with $x < 0.5$ are not complete superconductors [13,19]. Accordingly the problem of an appropriate identification of the samples becomes even more urgent if the thermodynamic characteristics are to be measured.

The thermodynamic properties of the $LnBa_2Cu_3O_{7-x}$ compounds shown in Table 1 were taken from several publications [12,14,15] and are in reasonable agreement. The heat capacity leap at the superconducting transition point was observed by all researchers who made the experimental measurements in the temperature range 50–150 K [3,4,6,12–15,19–38]. The absolute value of the leap differs from 2.3 to 5.5 J mol^{-1} K^{-1}, as well as its temperature interval (0.5–7 K) and the T_c value (79 K to 94 K). A review of a number of these publications has been made in ref. 39. The essential differences in these parameters can be attributed to the quality of the measured samples. For example, in ref. 5 the authors report different temperatures and absolute values of the leap as a function of the preparation method. In addition, some researchers [12,14,15] reported changes in the parameters after several heating–cooling cycles. This fact was ascribed to the non-equilibrium state of the samples immediately after preparation. In particular, the oxygen distribution might have been non-uniform, which leads to diffusion processes during the temperature recycling. It has been shown [12,14,15,32,38] that in the temperature range 45–83 K the $C_p(T)$ curve might exibit multiple maxima. This is probably caused by superconducting phase transitions for phases having different levels of oxygen non-stoichiometry. The C_p anomalies in these samples were in agreement with those found for electrical conductivity.

Heat capacity measurements at very low temperatures for this type of superconductor showed that: (1) $C_p(T)$ curves for the $LnBa_2Cu_3O_{7-x}$ compounds might have maxima at temperatures below 10 K; (2) the electronic term of the heat capacity may be described by a linear function.

While the first observation could be expected from the rare-earth properties, the second has no definite explanation (for $La_{2-x}M_xCuO_4$ compounds also). The low temperature C_p maxima were observed in refs, 3, 20, 39 and 41, and were ascribed to magnetic ordering [41]. The maximum values of the heat capacity for different rare earths were observed in the temperature range 0.5–10 K.

In a number of publications [15,19,40,42] to determine the Debye temperature a graphic approach was used. The value of θ_D was calculated from the slope of the $C_p/T = f(T^2)$ function, since according to the Debye model $C_p = AT^3$. If the heat capacity involves only the lattice term, these curves originate at zero in this co-ordinate system.

In the publications quoted extrapolation of the data to 0 K does not lead to a zero value for the function. This means that the heat capacity is described by a sum: $C_p = \alpha T + AT^3$. It should be noted that different authors give different values for α. Since the linear term of the heat capacity is attributed by some authors to non-superconducting impurities, the problem of analysis and characterization of the samples becomes even more urgent. In a number of publications the αT term is explained by the presence of oxygen-deficient phases or some other substances (for example, $BaCuO_2$ [28,41]). For example, in ref. 27 the heat capacity anomaly of Y–Ba ceramics was observed at 200–220 K. Some time later [41] this result was verified, and it was shown that the effect is caused by the lubricant used in the technology.

The authors of ref. 19 reported that the temperature dependence of the difference between the heat capacities of the superconducting and non-superconducting phases of $YBa_2Cu_3O_{7-x}$ and the sum of the heat capacities of yttrium, barium and copper oxides show a break at about 76 K, which can be ascribed to insufficient quality in measuring the thermodynamics of BaO [43]. This measurement was made in the temperature range 55–300 K. The number of experimental points was insufficient, and the reproduction of the results rather poor. The influence of impurities on the heat capacity of an yttrium superconductor was studied in refs. 23 and 41. It was shown that even small additions (up to 5%) of a trivalent metal led to a degradation in the heat capacity leap.

As a summary of the heat capacity results for superconductors of this type, two points should be stressed: (1) for single phase samples with a high oxygen index only one C_p anomaly is characteristic in the temperature range 10–300 K; and (2) there is no evidence that the linear heat capacity dependence at very low temperatures is connected with impurities rather than the substance itself.

Bismuth and thallium ceramics

Only a very limited number of publications deal with heat capacity of these materials [16,17,44–46]. All the measurements were made on multiphase samples, which is probably explained by a complicated preparation process. For this reason the reported data should be considered as rough estimates. The heat capacity curves for these samples involve several C_p maxima in the range 85–150 K. The properties of the samples are strongly dependent on the thermal processing [46]. The heat capacity data for bismuth ceramics are widely discordant. For example, according to refs 16 and 45 there is a linear term in the temperature dependence of the heat capacity, while in ref. 44 this term was not observed.

ENTHALPY OF FORMATION AND ENTROPY

Investigations of the thermodynamic properties of high-T_c superconductors are at the very beginning. The standard enthalpy of formation of Cu–Ba, Y and La oxides, as well as the ternary oxides, was measured [47,48] by calorimetric investigation of solution in $HClO_4$ [47] or HCl [48]. Depending upon oxygen non-stoichiometry, the value of $\Delta_f H^{\ominus}$ ($YBa_2Cu_3O_y$, s, 298.15 K), obtained in ref. 47 ranges from (-2671 ± 17) kJ mol^{-1} for $y = 6.25$ to (-2713 ± 17) kJ mol^{-1} for $y = 6.93$. Interpolation to $y = 6.5$ gives the value (-2675 ± 20) kJ mol^{-1} for the standard enthalpy of formation from the elements, or -143 kJ mol^{-1} for that from binary oxides (Table 2). The authors of ref. 48 reported values (Table 2) which strongly

TABLE 2

Enthalpy and entropy changes on formation of compounds from simple oxides

Compound	T(K)	$\Delta H(T)$ (kJ mol^{-1})	$\Delta S(T)$ (J mol^{-1} K^{-1})	Method	Reference
La_2CuO_4	298.15	−28	–	Calorimetry	47
$BaCuO_2$	298.15	−98.08	–	Calorimetry	48
	1000–1100	−53.8 ± 12.1	−17.9 ± 3.0	EMF	49
$Y_2Cu_2O_5$	298.15	−55.97	–	Calorimetry	48
	1100–1300	12.8 ± 1.7	18.4 ± 1.4	EMF	49
	1173–1340	20.7 ± 2.5	22.8 ± 2.7	EMF	50
	1097–1292	10.91	13.41	EMF	51
$YBa_2Cu_3O_{6\ 5}$	298.15	−143	–	Calorimetry	47
$YBa_2Cu_3O_{7-x}$	298.15	from: −154.6 to: −231.9	–	Calorimetry	48
	1073–1173	−66.6 ± 20.2	−9.4 ± 7.6	EMF	49
Y_2BaCuO_5	298.15	−78.3	–	Calorimetry	48
	1073–1173	−48.4 ± 11.9	−6.6 ± 2.1	EMF	49

depended on the method of preparation of the $YBa_2Cu_3O_{7-\delta}$ sample. These results are strongly discordant with the enthalpies of formation for $BaCuO_2$, $Y_2Cu_2O_5$ and Y_2BaCuO_5 from binary oxides given in ref. 47, also shown in Table 2.

The use of EMF methods [49–51] made it possible to obtain ΔH and ΔS for reactions of formation of substances from simple oxides at elevated temperatures. As can be seen in Table 2, these results are not in accordance with calorimetric data.

PHASE EQUILIBRIA

According to a review paper [52], in all the Ln–Ba–Cu–O systems $LnBa_2Cu_3O_{7-x}$ compounds were observed. The system Y–Ba–Cu–O has been studied in more detail (Fig. 1 [53]), although almost all the research concerned the $CuO–Y_2O_3–BaO$ section. The main experimental methods were X-ray diffraction, differential thermal analysis (DTA) and thermogravimetric analysis (TGA).

The $CuO–Y_2O_3–BaO$ section can be considered as a quasi-ternary system with compositional deviation from the triangular plane owing to non-stoichiometry.

In all the binary systems, oxides were found with 1 : 1 stoichiometry [52]: $Y_2Cu_2O_5$, Y_2BaO_4 and $BaCuO_2$. There are also other binary oxides having different compositions: $Y_4Ba_3O_9$ (Fig. 1, [53]), $Y_2Ba_4O_7$ [54], $Y_2Ba_2O_5$ [55], $BaCuO_3$ [54,55] and Ba_3CuO_4 [54]. The difference in the stoichiometrics of ternary oxides reported by different researchers is still more pronounced. In

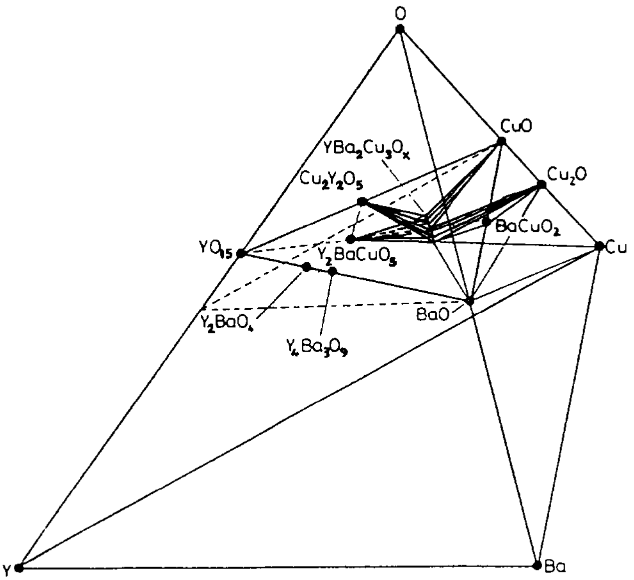

Fig. 1. Y-Ba-Cu-O system according to [55].

addition to the compounds $YBa_2Cu_3O_{7-x}$ and Y_2BaCuO_5 [52], some new substances were synthesised: $YBa_3Cu_2O_x$ [54,55], $Y_3Ba_8Cu_5O_{17.5+x}$ and $YBa_4Cu_3O_{8.5+x}$ [56], $Y_2Ba_3Cu_5O_{11+x}$ and $Y_2BaCu_3O_{7-x}$ [48]. Oxygen non-stoichiometry in oxides was studied using TG [53,56–58], mainly for $YBa_2Cu_3O_{7-x}$. The range of x in the formula was found to be $0 < x < 1$.

Owing to serious complications in the experimental studies of the four-component systems, special attention has to be given to thermodynamic simulation of phase equilibria. The first attempt to use this method for $YBa_2Cu_3O_y$ was reported in ref. 59. Because of the absence of suitable thermodynamic data for this system the authors of ref. 59 considered $YBa_2Cu_3O_y$ to be an ideal associated solid solution of simple oxides and $BaCuO_2$. It was shown that, depending on the model and compounds in the mixture, the y value may be limited to 6.5 at ~ 1300 K while at 1100–2000 K it increased up to 7.

We used the thermodynamic simulation method to reconstruct the phase equilibria in the Y–Ba–Cu–O system. All the published thermodynamic data for this system were used for this purpose. A direct thermodynamic problem was solved. The appropriate software was taken from ref. 60. The calculations were made at $P = 1$ atm, $T = 473$–1773 K.

In these calculations, the individual condensed phases having the properties given in Tables 1 and 2 were taken into account together with the ideal condensed solutions between simple oxides. Also, individual condensed and vapour phase compounds having the thermodynamic functions given in the database IVTANTERMO and thermodynamic tables [61] were considered.

A total of 13 condensed and 15 vapour phase compounds were involved. The calculations were made in 22 points of the concentration triangle CuO–Y_2O_3–BaO along the sections: $Y_2Cu_2O_5$–$BaCuO_2$, $Y_2Cu_2O_5$–Y_2BaCuO_5, Y_2O_3–$BaCuO_2$, CuO–Y_2BaCuO_5, CuO–$YBa_2Cu_3O_y$ ($y = 6.5$ and 7) as well as for the CuO–BaO and CuO–Y_2O_3 systems.

The calculations showed that the enthalpy of formation from the simple oxides reported in ref. 48 for $Y_2BaCu_3O_{7-x}$ (-116.8 kJ mol^{-1}) and $Y_2Ba_3Cu_5O_{11+x}$ (-284.2 to -343.04 kJ mol^{-1} for different preparation conditions) was in disagreement with all the published data on phase equilibria in Y–Ba–Cu–O: at 473–1573 K no existence field for $YBa_2Cu_3O_y$ was found within the CuO–Y_2O_3–BaO triangle. Also absent from the equilibrium mixture was the compound $Y_2BaCu_3O_{7-x}$. These measurements [48] were probably made on multiphase or non-equilibrium samples, and consequently were excluded from subsequent calculations.

There is a widespread opinion that the high-T_c superconductors are thermodynamically metastable substances (see, for example, ref. 62). On the other hand, it is well known that prolonged sintering at 1073 K in oxygen or in air stabilizes the $YBa_2Cu_3O_y$ compound [52]. Since the ΔH and ΔS values reported in refs. 49–51 for reactions for formation of $BaCuO_2$ and $Y_2Cu_2O_5$ from simple oxides are in agreement with each other, and the absolute standard entropy of $YBa_2Cu_3O_{7-x}$ is also known (Tables 1 and 2), it was interesting to estimate the minimum value for the formation enthalpy of $YBa_2Cu_3O_{7-x}$ which would ensure the thermodynamic stability of this compound at $T \geqslant 1073$ K. The corresponding calculations showed that the low temperature limit of stability for $YBa_2Cu_3O_{7-x}$ is 1073 K if

TABLE 3

Equilibrium condensed phases (in mol kg^{-1}) for the overall composition $YBa_2Cu_3O_{6.5}$

T (K)	Individual phases			Solution		
	Cu_2O	$BaCuO_2$	$YBa_2Cu_3O_{6.5}$	BaO	Y_2O_3	CuO
473	1.473×10^{-6}	1.8231	–	2.04×10^{-5}	0.45580	0.91156
573	1.473×10^{-6}	1.8229	–	2.162×10^{-4}	0.45583	0.91176
673	1.473×10^{-6}	1.8220	–	1.144×10^{-3}	0.45579	0.91269
773	1.475×10^{-6}	1.8191	–	3.9725×10^{-3}	0.45572	0.91551
873	1.815×10^{-6}	1.8126	–	1.0508×10^{-2}	0.45574	0.92204
973	2.1083×10^{-5}	1.7999	–	2.316×10^{-2}	0.45577	0.93466
1073	–	6.058×10^{-7}	0.91152	3.244×10^{-8}	3.5766×10^{-7}	3.5146×10^{-7}
1173	–	–	0.91152	2.315×10^{-8}	1.4632×10^{-7}	6.676×10^{-8}
1273	–	–	0.91152	1.3645×10^{-7}	2.3262×10^{-7}	5.6675×10^{-8}
1373	–	–	0.91152	2.0623×10^{-6}	7.2706×10^{-7}	2.8093×10^{-7}
1473	–	–	0.91128	5.208×10^{-4}	1.3056×10^{-4}	5.9772×10^{-5}
1573	–	–	0.9106	1.8403×10^{-3}	4.6152×10^{-4}	1.9508×10^{-4}
1673	1.1485×10^{-2}	–	0.90296	1.7123×10^{-2}	4.2886×10^{-3}	1.6371×10^{-3}
1773	4.2417×10^{-2}	–	0.87988	6.314×10^{-2}	1.5823×10^{-2}	6.3218×10^{-3}

TABLE 4

Equilibrium condensed phases (in mol kg^{-1}) for the overall composition ($0.5CuO + 0.5YBa_2Cu_3O_{6.5}$)

T (K)	Individual phases			Solution		
	Cu_2O	$BaCuO_2$	$YBa_2Cu_3O_{6.5}$	BaO	Y_2O_3	CuO
473	1.538×10^{-6}	1.6265	–	2.5286×10^{-5}	0.40664	1.6265
573	1.538×10^{-6}	1.6263	–	2.6792×10^{-4}	0.40661	1.6268
673	1.538×10^{-6}	1.6251	–	1.4174×10^{-3}	0.40668	1.6279
773	1.542×10^{-6}	1.6216	–	4.9195×10^{-3}	0.40659	1.6314
873	2.2429×10^{-6}	1.6135	–	1.3×10^{-2}	0.40660	1.6395
973	4.1834×10^{-5}	1.5979	–	2.8598×10^{-2}	0.40663	1.6550
1073	1.279×10^{-3}	0.89490	0.34636	3.893×10^{-2}	0.23346	1.3165
1173	3.218×10^{-2}	3.7648×10^{-2}	0.77876	3.136×10^{-2}	1.7252×10^{-2}	0.81476
1273	0.31619	–	0.80882	8.893×10^{-3}	2.223×10^{-3}	0.19422
1373	0.40663	–	0.81326	7.393×10^{-11}	7.078×10^{-10}	1.363×10^{-9}
1473	0.40663	–	0.81326	1.165×10^{-9}	1.161×10^{-8}	9.257×10^{-9}
1573	0.40659	–	0.81326	2.14×10^{-8}	1.55×10^{-7}	6.42×10^{-8}
1673	0.40639	–	0.81326	3.76×10^{-7}	1.662×10^{-6}	4.11×10^{-7}
1773	0.40554	–	0.81324	5.512×10^{-6}	1.385×10^{-5}	2.842×10^{-6}

$\Delta_f H^{\ominus}(YBa_2Cu_3O_{7-x}$, s, 298.15 K) is -2596 kJ mol^{-1}, which corresponds to -62 kJ mol^{-1} for the enthalpy of formation from simple oxides. As an example Tables 3 and 4 show the equilibrium compositions calculated in two points of the compositional triangle $YBa_2Cu_3O_{6.5}$ and ($0.5CuO + 0.5YBa_2Cu_3O_{6.5}$). It can be seen from a comparison of the Table 3 data with that given in Tables 1 and 2 that the accepted value for $\Delta_f H^{\ominus}(YBa_2Cu_3O_{6.5})$ leads to thermodynamic metastability of this compound below 1073 K, while at $T > 1073$ K its stability is due to the entropy term.

To summarize, it should be noted that in spite of a large number of publications on phase equilibria in oxide systems with high-T_c superconductors the situation is not at all clear. The final solution of this problem can be based only on the complete thermodynamic characterization of all the substances involved.

APPENDIX A

Three of us (Lazarev, Nadtochii and Shaplygin) report the latest results on thermal conductivity and thermoelectric power of the textured ceramic high-T_c compound $Bi_2Sr_2CaCu_2O_{8+\delta}$.

Measurements of resistivity, thermal conductivity and thermoelectric power on this superconductor have been carried out. Quenching of the superconductor causes unit cell deformation along the tetragonal axis at constant cell volume. Oxygen loss within $\Delta\delta \approx 0.1$ during the process and elongation of the c axis inside the ratio $\Delta c/c \approx 0.003$ take place. In the optimal conditions determined there is a successful chance of T_c increasing by ~ 20 K. This fact is connected with initial lattice deformation. The deformation mechanism and its influence on the band structure is also discussed.

The bismuth based oxide, a new class of high-T_c superconductor, has created opportunities for conducting comparative studies [63]. High-T_c superconductors in the Bi–Sr–Ca–Cu–O system are more stable than 1 : 2 : 3 compounds, and there probably will be other mechanisms of superconductivity.

The $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) sample was prepared by solid state reaction from a mixture of evaporated Bi, Sr, Ca and Cu nitrates at 820 °C for 50 h in air [2]. Chemical analysis of the phases has been carried out by atomic absorption spectroscopy [64]. The oxygen content was measured by the gas-volumetric method [65]. For the phase $Bi_2Sr_2CaCu_2O_{8+\delta}$ δ varied as $0.4 \leqslant \delta \leqslant 0.6$. Pseudotetragonal cell parameters from X-ray powder diffraction data are: $a = 5.40$ Å and $c = 30.9$ Å.

BSCCO pellets ($8 \times 3 \times 2$ mm^3) or disks (diameter 10 mm, thickness 1.5–2.0 mm) were calcined at 820 °C for 8 h and cooled to room temperature at the rate 7 K min^{-1}. Pellets were subjected to resistive measurements and disks to thermal conductivity and thermal electrical power measurements. Both pellets and disks were textured with the preferred orientation of crystallites along the c axis by a pressure procedure.

Under the synthetic conditions, the resistive superconducting transition curve gave T_c value near 65–70 K. In optimal conditions before quenching the sample having an initial value of $\rho = 1.3 \times 10^{-3}$ Ω cm was annealed at 830 °C for 3–4 h and then quenched in liquid nitrogen; it gave a T_c value near 90 K with initial resistivity of 4×10^{-3} Ω cm. The mass change of the sample because of oxygen loss was $\Delta m/m$(initial) 0.2%, corresponding to $\Delta\delta \approx 0.1$. After quenching the unit cell of BSCCO was elongated a little along the tetragonal c axis at constant cell volume. The relative increase in the c parameter was $\Delta c/c \approx 0.003$. The effect of quenching causes hysteresis— on annealing at 500 °C for 7–8 h the transition temperature returns from 90 K to the initial value of 68 K, and $\rho = 1.28 \times 10^{-3}$ Ω cm. The sample mass has no hysteresis and oxygen evaluated at quenching does not recombine in BSCCO, but the cell parameters were the same as initially (the original and unique fact!).

At quenching temperatures of 300 °C, 500 °C and 700 °C BSCCO samples usually have no oxygen loss (i.e. $\Delta\delta = 0$). The increase in T_c can thus be explained as a result of lattice deformation. The decisive role of lattice deformation as a consequence of quenching is evident. We note that the super-stoichiometric oxygen content in BSCCO is an important feature of resistivity in the normal state of BSCCO. In the region $T > 2T_c$, resistivity is described by $\rho(T) = A + BT$ (where A is the residual resistivity and B is a linear term), i.e. the quenching causes the superconducting system to approach the metal–insulator transition.

The thermal conductivity and thermoelectric power of BSCCO are connected with the porosity of the samples. From experimental results it is obvious that quenching decreases the thermal conductivity of the specimens by up to 10–15% from the initial one. From the Wiedemann–Franz law we have estimated the upper limit of free carriers in bulk thermal conductivity, which is equal to ~ 10% at 100 K, in the manner of ref. 66. It may be stated that phonons are responsible for thermal properties. We give an equation $\lambda \approx CS^2\tau$, where C is the phonon heat capacity, S is the velocity of sound, $\tau^{-1} = \tau_{\mathrm{ph,l}} + \tau_{\mathrm{ph,d}} + \tau_{\mathrm{ph,ph}} + \tau_{\mathrm{ph,e}}$, and $\tau_{\mathrm{ph},x}$ are relaxation times connected with phonon scattering on grain boundaries, lattice defects and dislocations, phonons and electrons, respectively. Relaxation time estimation is based on heat capacity data for ceramic samples $Bi_2Sr_2CaCu_2O_{8+\delta}$ [16] where the Debye temperature was 470 K near 100 K. The S value is estimated from the ratio $S = k\theta/\hbar^3(6\pi^2N)^{1/2}$, where $N = 15N_A$ G mol^{-1} and N_A is Avogadro's number (from $S = 3.8 \times 10^5$ cm s^{-1}). Estimated values of relaxation times at 100 K are (10^{-14} s): $\tau_1 = 7.3$; $\tau_2 = 6.4$; $\tau_3 = 4.65$; $\tau_4 = 3.96$; $\tau_{1,\mathrm{ph,e}} = 23.5$; $\tau_{2,\mathrm{ph,e}} = 109$; $\tau_{3,\mathrm{ph,e}} = 16.3$; and $\tau_{4,\mathrm{ph,e}} = 116$. We emphasize that quenching of BSCCO samples having a T_c value of 90 K have a phonon–electron relaxation time τ_{ph},e $\approx 10^{-12}$ s, the same as for $YBa_2Cu_3O_{7-\delta}$ with $T_c = 90$ K [66]. Oxygen loss and lattice deformation increase the ratio $\tau_{4,\mathrm{ph,e}}/\tau_{3,\mathrm{ph,e}}$ up to ~ 7 at quenching. After annealing of the samples the lattice dimensions reduce, giving a ratio $\tau_{2,\mathrm{ph,e}}/\tau_{1,\mathrm{ph,e}}$ of ≈ 24.6.

At increasing time $\tau_{\mathrm{ph,e}}$ can influence the density of electron states on the Fermi surface and can decrease the level of phonon–electron scattering. In the thermal dependence of thermoelectric power there are two regions. With the coexistence of positive and negative terms together with a negative temperature-dependence term, we can probably explain both p and n carrier types in BSCCO. This theory is confirmed by zone band calculations [67].

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