EFFECTS OF 123–EXPANSION

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The most general description for the thermal expansion of solids is a change of macroscopic strain parameter with temperature [1]:

$$\alpha_{ik} = (\partial \varepsilon_{ik} / \partial T)_p ;$$

tensor α_{ik} is linear thermal expansion coefficient (CTE). The trace of matrix defines volume thermal expansion coefficient β :

$$\beta = (\partial \ln V / \partial T)_p ;$$

which relates to α in isotropic case as

$$\beta = 3\,\alpha = 3(\partial \ln l / \partial T)_p$$

(here V, l and P are volume, length and pressure, respectively).

Temperature dependencies of thermal expansion parameters contain information on dynamical processes in crystals on microscopic scale, they are connected to the macroscopic parameters of phase transformations in solids and determine the level of thermo-elastic streses. Consequently, investigations of thermal expansion are available both for fundamental and technical reasons.

Thermal expansion peculiarities of high temperature superconductors (HTS) are caused by their complicated structure, dependent on the conditions of synthesis. The need in detailed study of the related effects is determined by a number of reasons: anisotropy of HTS properties originated from their layered structure which results in high thermal stresses, high sensitivity of their superconducting properties to Cu–O bond length and cell parameters, structural transformations accompanied by lattice volume changes; oxygen redistribution and associated elastic stresses the elastic effects in magnetic flux pinning.

1. Thermal expansion of superconductors. The fundamentals of thermal expansion treatment were founded by Mi–Gruneizen works for phonon subsystem , characterized by the single vibration frequency which is determined by central interatomic interactions. The basic dimensionless relation is:

$$\gamma = \beta V / \chi_T C_\gamma ;$$

γ is temperature independent Gruneizen parameter. For complicated structures like HTS this model is valid for low temperature (about few percents of Debye temperature $\Theta_D \approx 400$ K) [2]. CTE is defined by the ratio of free energy derivatives its additivity at low temperatures results from the weak temperature dependencies of volume modules: $\beta = \sum_r \beta_r = \chi_T \sum_r (\partial S_r / \partial V)_T^\gamma$ is not additive function but a follows one of different contributions [3]:

$$\gamma = \sum_k \gamma_k C_k / \sum_k C_k ;$$

C_k is heat capacity of each contribution related to lattice, electron ones and so on. The statistical mechanics suggests relation of $(\partial S / \partial V)_T$ and consequently $\gamma(T)$

with the energies of quantum states in solids. So experimental values of γ are useful for analysis of strain dependencies of T_c, with respect to Eliashberg–McMillan equation. Superconductivity is collective ordering processes in electron subsystem and superconducting transition effects superconductors free energy. Corresponding changes of V, l, α and β in the normal (N) and superconducting (S) states are thermodynamically related to critical superconducting parameters — bulk critical field H_c, critical temperature T_c and their derivatives. Thermodynamics of superconductors with respect to bulk critical field dependence on the stress distribution was discussed for hydrostatic compression in [4]. [5] presents equations for the changes of α at T_c in crystals with different symmetries. The next relations were obtained [4] for type I superconductors but were sucsessfully applied to type II ones and HTS:

$$V_N - V_s(0) = V_s \frac{H_c}{4\pi} (\partial H_c/\partial p)_T + \frac{H_c^2}{8\pi} (\partial V_s/\partial p)_T;$$

$$l_{N_i} - l_{s_i}(0) = l_{s_i} \frac{H_c}{4\pi} (\partial H_c/\partial \sigma_i)_T + \frac{H_c^2}{8\pi} (\partial l_{s_i}/\partial \sigma_i)_T;$$

σ_i is uniaxial stress in i-direction. The right part contains small magnetostriction contribution (last terms). Apparently at H_c

$$\beta_N - \beta_s = (1/4\pi)(\partial H_c/\partial T)_p (\partial H_c/\partial p)_T;$$

$$\alpha_{N_i} - \alpha_{s_i} = (1/4\pi)(\partial H_c/\partial T)_p (\partial H_c/\partial \sigma_i)_V.$$

It suggests at $T = T_c$:

$$\beta_N - \beta = (C_N - C_s)/V(d\ln T_c/dP)$$

(C_N and C_s are specific heat capacities at constant pressure in N and S states), which is easily transformed to Erenfest relation for second order phase transition. $\Delta\alpha$ measurements present sufficient advantage for HTS [6] as the C_p electron-component jump is small for then, comparatively to phonon background: 3–4 % C_p for 123 and even less for substitutions. $|\Delta\alpha/\alpha|_T = \Delta C_p/C_p$ at $dT_c/dP \simeq 0.1$ K/bar and at $dT_c/dP > 0.1$ K/kBar. CTE-measurements are more sensitive. Besides it provides means for registration of structural changes at T_c independent of $S-N$-transition. Respectively CTE-measurements are used for investigation of the critical parameters dependencies on strain. Comparative analysis of the data for conventional and HTS-conductors suggests analogies of the latter with compounds of A15-type, which are structurally unstable and posses high α, strongly dependent on stoichiometry [7]. Effects of structural phase transitions may be revealed in CTE-measurements [8]. The rate of volume changes at structural transformation is proportional to the rate of phase composition change. Temperature spectrum of the volume effect for reversible first order transition in nonithothermal regime depends on the rate of temperature variation and atoms mobility. At second order phase transitions volume changes reveal in temperature dependence of α at continuous variation of T.

2. Experimental technique. By technical reasons the comparative analysis of numerous data on CTE is available only for ceramic HTS. We studies ceramic

samples of 123 obtained by powder technique, which alowed to produce rods of 65 mm length. Experiments on ceramics nesseciated careful attention to the porosity and grain size effects in the temperature dependence of measured CTE. The grain size was estimated in optical microscope. The comparative porosity of the samples was approximately evaluted according to Table 2, which presents parameters related to CTE for HTS of various porosity [9]. Important structural feature of HTS effecting its characteristics is oxygen stoichiometry and distribution which is especially difficult for control. Here it was controlled according to indirect data on synthetic parameters and T_c measurements. The state of the impurities and defect structure evolution in the process of low temperature treatment were controlled with the help of trapped magnetic flux measurements [10,11]. This method combined with direct structural and magnetic investigations provides data on the magnetic and defect structures interaction [12, 13], particularly, for high temperature superconductors. Thermal expansion measurements were used for estimation of CTE and thermal stress [14, 15] in the sample tested at low temperatures. Linear coefficient of thermal expansion (TEC) was registered in the range of temperatures 80–500 K by differential technique (Fig. 1), involving thermostabilized electronic registering unit and displacement probe. The probe action is based on eddy current induction in pick up plate placed in h.f. field of the coil and dependent on the distance between then. Eddy currents induced in the plate define coils quality, factor wich changes with the distance between the coil and the plate

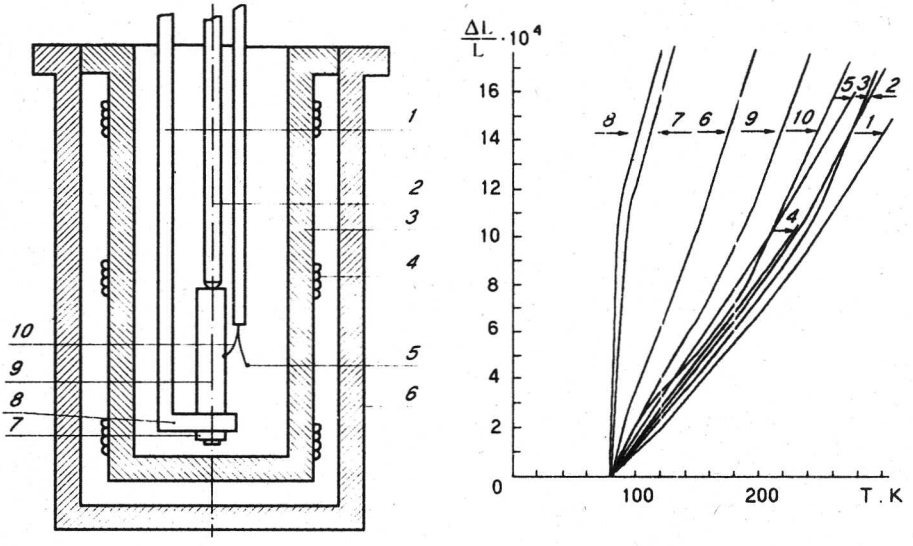

Fig. 1. Schematic presentation of the dilatometer test unit-bearing Invar bar, *2* — Invar rod, *3* — internal bushing, *4* — spiral heater, *5* — setting thermocouple, *6* — external bushing, *7* — screw nut, *8* — Invar platform, *9* — sample, *10* — measuring thermoelement

Fig. 2. Thermal expansion of 123 after different treatments

and provides the main output signal of the probe. For thermostabilization of the sensing unit the thermocryocell immersed in cryoagent was used. The temperature of the sample was measured with special thermoelement. The data on elongation and temperature were registered on the single graph. Elongation was measured with

accuracy better than 0.3 μm . The pores effect thermal expansion by two ways — creating the volume part with CTE different from the matrix and due to elastic stress distribution. The latter along with the thermal stresses near the grain boundaries of differently oriented crystallizes in these anisotropic structures reguire careful control of homogeneous temperature distribution in the sample during CTE measurement. TEC-measurements were checked on by two ways-in stationary regime with thermocell achieving fixed temperature point and in regime of program-controlled temperature regulation with fixed heating rate 0.1–1 grad/min. Coincidence of the results obtained in two regimes suggests continuous thermal run of samples linear dimension with minimal temperature gradients wich garanties structural homogeneity and simultaneity of morphological transformations and relaxation transitions with temperature change.

3. Results and discussion. The results obtained for $\Delta L/L$ of 123 are presented in Fig. 2. Apparently there are some peculiarities for the samples after different treatments. It suggests structural effects in thermal expansion.

As different structural features influence CTE of 123 we tried to divide their contributions to experimental results with respects to the data published previously.

3.1. Oxygen effects. Equilibrium oxygen stoichiometry of $123\,x = 6.2$ is realized at 900 °C and 1 atm of oxygen. To obtain $T_c > 90$ K oxygen content must be rised to $x \simeq 6.98$ by low temperature aging. Total oxygenization of dense ceramic requires oxygen diffusion along grain boundaries and across grains with $x = 7$. As result the rate of oxygenization decreases while the specific volume of oxygenated layer remains larger or equal to nonoxydized ceramics layer. Unit cell volume of 123 is strongly dependent on the oxygen stoichiometry which can be easily changed. Introduction of oxygen in 123 results in the absence of screening for Cu-atoms nearby to interstitial oxygen and related increase of their interaction with CuO_5 pyramidal oxygen. Presumably it causes lattice compression with oxygenization. This effect may result in reversible expansion dependent on composition. Accompanying elongations are often larger than compositional expansion. Thermal and compositional effects superimpose at temperature dependent change of stoichiometry. They may be divided by the next way. Heating of the sample with $x \approx 6.2$ in the temperature range 25–800 °C in nitrogen results in $\alpha \simeq \text{const} \simeq 10.7 \cdot 10^{-6}\,°C^{-1}$. Oppositely, heating of the sample with $x \simeq 7$ in the air at first $\alpha \simeq 12.9 \cdot 10^{6}\,°C^{-1}$ and in temperature range 450–600 °C — increased. This temperature and pressure range coincides with the one of deoxygenization of 123 and large compositional component is available. Coiling in oxygen atmosphere results in compositional compression. This component may be identified by dilatometry at constant temperature in different atmospheres [16]. At temperatures 450–600 °C thermal expansion features results from the change of oxygen content. At temperatures $T < 300$ °C structure cannot loose oxygen to the opinion of the number of the authors, and volume changes result from the common thermal expansion or phase transitions. The results of [17] also prove effect of CuO-excess on bulk properties.

Dilatometry was used for investigation of oxygen diffusion in tetragonal $Y_1Ba_2Cu_3O_{7-\delta}$ [18] . Observed kink on temperature dependence of volume at 411 °C resulted from competing effect of lattice parameter increase at heating and unit cell volume decrease of the quenched sample at elevated temperatures, related to tetra-ortho transition initiated by introduction of oxygen into the lattice. At constant temperature tetra-ortho transition is controlled by oxygen diffusion. It allows to estimate parameters of the process from dilatometric measurements.

Activation energy of oxygen diffusion was estimated in [18] as 17690 kal/mol. Long term diffusion and small particles allow to produce materials with high j_c.

3.2. Substitution effects. Substitution of different elements in ittrium HTS study sufficiently influenced the understanding of physical processes in this material. The associated effects must be always taken into consideration by technological reasons. For example small amounts of Al-addition, which is often present in crucibles, may essentially effect properties of 123 in normal and superconducting state. Particularly T_c drastically decreases at substitution of Cu over 1 %. Thermal expansion is more sensitive probe of *SN*-transition for substituted 123 than heat capacity because of large dT_c/dP -values (0÷0.05 K/kbar for 123 and 0.5 K/kbar for Fe, Co, Al-substitutions) with respect to Erenfest equation presented above. Analysis carried out in [6] justifies electronic character of $\Delta\alpha$ at T_c for 123 compound as well as for the one with Cu-substitution and its superconducting nature. For comparison, this equation is not fullfilled for A15-compounds because of structural transition and value $\Delta\alpha$ is one order higher than expected for *SN*-transition.

Ittrium substitution by the other rare earth elements was systematically studied [2, 19] in magnetic field up to ~ 20 T. Phase transition induced anomalies at T_c were not observed. All temperature dependencies of thermal expansion may be reduced to the one for unsubstituted compound which proves the same nature of lattice phonons. Magnetostriction anisotropy was observed only for Dy and Ho-substitutions. For Eu, Sm, Gd, Er, Tm, V magnetostriction is small similarly to nonmagnetic superconductors. Presumably in the first case magnetostriction was observed in normal cores of vortices and not registered for the materials with the magnetic fields corresponding to entirely diamagnetic state. [20] present volume jumps at $T = T_c$ observed for Zr-doped ittrium ceramics by *X*-ray technique. Analysis of structural and thermophysical data suggested effect of structural transition.

3.3. Effects of lattice instabilities. Possible related of high temperature superconductivity with lattice instabilities similarly to A15 compounds was investigated by CTE measurements for orthorombic and tetrahonal 123-modifications. Anomalies at 205 K were observed for orthorombic modification and in 92–130 K — range for tetrahonal one [21].

Manifestations of structural transition in 123 at 240 K were observed by CTE, ultrasonic, acoustic, heat capacity, specific heat, resistivity, structural measurements (see for example [5]). Explanation of anomalous CTE-component at temperatures above T_c is not obvious. The possible explanation is associated [22] with bipolaronic coupling.

X-ray [23–25], dilatometric [26] and neutron diffraction investigations revealed at T_c change of the slope for $\alpha(T)$, and [27,28] have shown large volume changes. $\alpha_{min}(300\ \text{K}) = 11.5 \cdot 10^{-6}\text{K}^{-1}$, close results were obtained in [25–27].

3.4. Effects of structural anisotropy. HTS — anisotropy suggests effects of uniaxial stresses induced by anisotropic thermal expansion. Systematic investigation of thermal expansion anisotropy of single crystals and textured ceramics 237 was carried out in [28]. There were observed distinct jumps on the temperature dependencies of α in *ab*-plane at the same temperatures as heat capacity. In *c*-axis direction the jumps were not observed. Comparison of the data [29] for single crystals and ceramics have shown that the values measured during heating in the temperature range 100–300 K coincide with the CTE of the lattice, obtained for

ceramics by X-ray technique, as well as with dilatometric data. CTE-values measured during cooling are much higher.

4. Thermodynamical analysis of thermal expansion data for 123 near T_c. The analysis is based on free energy F equation in the normal and superconducting states with respect to its strain dependence [5]. This treatment was applied to A15 [7] and it was shown that at T_c the strain jump takes place which drastically decreases increase of strain related to structural transformation. It means that generation of superconductivity postpones further structural transformations.

The results of CTE measurements for 123 in most cases prove superconducting transition nature of the anomaly at T_c. The negligible softening of longitudinal optical phonons associated with atoms vibration in CuO_2 — plane observed at superconducting transition cannot have sufficient effect on bulk parameters because of their high frequencies. There are no evidence of the marked changes at $T = T_c$ in the other quasipartical spectra. Thus $\Delta\alpha$ may result from the changes in electronic spectrum. For Fermy — degenerated conduction electrons Gruneizen equations is valid at $kT << \varepsilon_F$, i.e. not only at T_c, but also at sufficiently higher temperatures. Consequently, description of CTE in the vicinity of SN-transition may include Gruneizen parameter similarly to metallic superconductors [30]. Experimental values of γ satisfactorily agree with the calculated ones [31] from bulk equations and interatomic potential for ionic crystals. Technique for analysis of structural evolution developed in [32] on the basis of bulk equations applied to modeling of thermal expansion anomaly near T_c allows to divide elastic and structure transformation contributions. The results for 237 ceramics have shown effect of local strains presumably associated with thermal stresses near boundaries of anisotropic grains at thermocycling. Thermal expansion measurements are useful for evaluation of T_c dependence on hydrostatic pressure dT_c/dP. They exclude problems of heterogeneous uniaxial compressions, surface effects and influence of structural transformation while C_p data are concerned. Investigation of the critical parameters dependencies on strain is important for the analysis of connection between superconductivity and materials microstructure. $dT_c/dP < 0$ for conventional nontransition-metals based superconductors as pressure increases elastic stiffness, Debye temperature and average phonon frequency. In conventional transition metals based superconductors the derivative sign may change for competing increase of T_c with increase of ionic potential. dT_c/dP for oxide HTS one or two orders higher than for conventional superconductors [33]. $T_c(P)$ dependence of conventional superconductors was not explained satisfactorily.

HTS-conductors may be divided in two groups: the first — with higher T_c (123, Bi–Tl-compounds) and $dT_c/dP \approx 0-0.02$ K/GPa ; the second — with lower T_c (La–M–Cu–O–) with $dT_c/dP \approx 0.09$ K/GPa [34]. The place of 123 has changed after observation of $T_c(P)$ — increase in Eu-substituted oxygen deficient compound ($T_c = 60$ K) and the absence of this effect in stoichiometric compound. It was also shown that 124-compounds with higher T_c(80 K) may as well have strong pressure dependence of T_c. The lowest value of dT_c/dP for 237-compound, suggests dependence of dT_c/dP oxygen content. It worth to note prominent difference of the data that may be explained by experimental conditions. Declination

from hydrostatic pressure may induce high shear stresses in highly anisotropic HTS-structures resulting in cold working of the sample, widening of superconducting transition and modification of $T_c(P)$. It is known that in A15 nonhydrostatic pressures may initiate the change of the sign [33].

dT_c/dP, measured for $Y_1Ba_2Cu_3O_{7-\delta}$ differ in the range -0.8 – 4.3 K/GPa [35,36], $dT_c/d\sigma_{ij}$ — even more [28, 37, 38]. For compositions close to stoichiometric ($\delta = 0$) the measured dT_c/dP are 0–1.3 K/GPa. Continuous increase of T_c with P is quite obvious $T_c/dP = +$ (0.5–0.7) K/GPa in the range of "low" pressures (up to 2 GPA) [39–43]. dT_c/dP data descripancies may be connected not only to shear stresses but also to different oxygen content and the derivatives relative values may be used for its approximate estimation.

The results on thermal expansion anisotropy presented previously suggest the connection of pressure effect with displacement of oxygen atoms to the sites corresponding to high T_c; as a result the pressure effect weakens for compositions near stoichiometric. Neutron diffraction measurements under pressure revealed oxygen displacement from Cu(1) in the chains to Cu(2) in the planes, which induce increase of carriers concentration in superconducting planes.

Concluding remarks. Thus low-temperature thermal expansion measurements of 123 ceramics produced in different conditions reveal effects of structural features. CTE are sensitive to thermal treatment, grain size and anisotropy level of the granular conglomerate. Possible explanation of the latter is high anisotropy of CTE in 123.

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