First and second order phase transitions in $YBa_2Cu_3O_{6+x}$ due to redistribution of oxygen along the chains at low temperatures

L. G. Mamsurova, K. S. Pigal'skiĭ, V. P. Sakun, A. I. Shushin, and L. G. Shcherbakova

N. N. Semenov Institute of Chemical Physics, Academy of Sciences of the USSR

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By using a model which takes exact account of intrachain thermodynamics and interchain interactions, and by the mean field method, it has been shown that the orthorhombic structure of high-temperature superconductors (HTSC) $YBa_2Cu_3O_{6+x}$ allows four stable phases to exist which differ in respect of the type of oxygen ordering along the chains in the basal plane. Both first and second order phase transitions are possible in this case between the structural modifications of the orthorhombic lattice. An explanation is given, based on the T–x diagram, of the experimental temperature dependences of Young's modulus and acoustic losses at $T < 300$ K for $YBa_2Cu_3O_{6+x}$ specimens containing different amounts of oxygen

INTRODUCTION

On the basis of an analysis of experimental results, the suggestion has been made in a number of earlier articles (for example, Refs. 1–4) of a non-uniform nature in the distribution of the superconducting phase in $YBa_2Cu_3O_{6+x}$, associated with a non-uniform distribution of oxygen. Not only was the non-uniformity borne in mind which must be found in ceramic specimens resulting from the existence of boundaries between the grains or in single crystals because of twin boundaries, but also the non-uniformity existing within the body of a domain of the orthorhombic structure. In studying high T_c superconductors (HTSC) of the composition $YBa_2Cu_3O_{6+x}$ by high-resolution electron microscopy, the existence of considerable local regions with double or even with triple crystal lattice period[5-7] on a background of correct orthorhombic structure is, in fact, noted. Sometimes doubling of the elementary cell along the **a** axis appears to be characteristic of the whole single-crystal studied.[6] Kemin *et al.*[8] reported on the existence in $YBa_2Cu_3O_{6+x}$ of other exotic substructures also, for example such as where the elementary cell is oriented at an angle of 45° to the orthorhombic basis, etc.

The question arises: does the orthorhombic structure of $YBa_2Cu_3O_{6+x}$ allow within itself such a variety of substructures or is it a question of the realization of some metastable phases thanks to the existence of some other sort of defects in the synthesis of $YBa_2Cu_3O_{6+x}$?

There are some publications in which theoretical analysis of the T–x phase diagram of these materials has been carried out.[9-15] In these papers the phase transformations in $YBa_2Cu_3O_{6+x}$ are associated with the redistribution of oxygen over sites in the CuI–O4 basal plane. Kubo *et al.*[9] carried out a calculation of the thermodynamics of the high-temperature "tetra–ortho" transition of a $YBa_2Cu_3O_{6+x}$ crystal of non-stoichiometric composition, in the mean field approximation. A similar method was used by Nakamura and Ogawa[10] and by Khachaturyan *et al.*[11] Apart from the calculation of the tetra–ortho transition curve, the existence of a low-temperature region of decomposition of the tetra and ortho phases was shown,[11] and also the possibility of the coexistence in a narrow temperature range of two other phases "of the same structure, but with different oxygen content." Khachaturyan and Morris[13] suggested the kinetics of the decomposition of the phases, according to which a number of Magneli-type phases arise sequentially in the process of decomposition. More exact calculations carried out by Zubkus *et al.*[15] using the gas-lattice method, taking account of the interaction between nearest neighbors, showed however that two-phase regions are evidently exceptionally narrow and are localized at such small values of x which are of no special interest for HTSC. Similar results were obtained[12,14] by the cluster variation method (the T–x phase picture for $YBa_2Cu_3O_{6+x}$ shown by Wille *et al.*[12] contains expanded low-temperature sections of differentiated phases, but they are of a speculative nature and therefore less certain that in Zubkus *et al.*[15]). A theoretical basis for the existence of a substructure with doubled period along the **a** axis is given by Nakamura and Ogawa,[10] Wille *et al.*[12] and by Zubkus *et al.*,[15] the so-called ortho-II phase which had already been predicted in the early stages of the investigation of HTSC[16] on the basis of the dependence of T_c on x.

Theoretical analysis so far thus limits the structural variety of the compound $YBa_2Cu_3O_{6+x}$ to the existence of three different phases: a tetragonal and two orthorhombic, ortho-I and ortho-II.

It should be noted that there is now a real possibility of only a highly approximate theoretical consideration of the phase diagram of $YBa_2Cu_3O_{6+x}$. This is already clear from the fact that contrary to experiment, the theories[9-15] allow in principle all values $0 \leqslant x \leqslant 2$. The suggestion of additivity and x-independence of the parameters of the interparticle interaction in a system of variable valency (as the basal plane is filled with oxygen, Cu^+ transforms into Cu^{3+}) is also a considerable limitation. There is too an appreciable arbitrariness in the choice of the parameters of the interparticle interaction; in particular the choice made[12,14,15] is highly debatable (see below).

The aim of the present work is a search for possible stable ordered structures in the distribution of oxygen ions along chains in the basal plane in the low-temperature region, and for values of x most realistic for HTSC ($x > 0.5$), starting from the experimental data available and on the basis of the simplest physical considerations. We are not then aiming to construct any complete phase diagram for $YBa_2Cu_3O_{6+x}$. A number of approximations (for example,

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the independence of pair interparticle interaction of x and its additivity) have also been made in the theory proposed. It will be shown that the orthorhombic structure of the compound $YBa_2Cu_3O_{6+x}$ allows for the existence of several stable phases differing from one another by the different type of ordering of the oxygen along the CuI–O4 chains, between which phase transitions of both first and second order are possible as the temperature is lowered.

THEORY

The main premise of the theory presented in the present work is the experimental data, which indicate the existence of phase transitions in $YBa_2Cu_3O_{6+x}$ occurring at $T \approx 1000$ K and $T \approx 240$ K.

It is known that the phase transition at $T \approx 1000$ K is associated with ordering of oxygen ions on sites on the CuI–O4 basal plane, accompanying transformation of the tetragonal structure into orthorhombic.[9] A number of anomalies in the physical properties of the material accompany this transition, in particular a marked peak in acoustic losses.[17] Roughly the same form and magnitude of the loss peak is also observed at a temperature $T \approx 240$ K (Refs. 18,19). The independence of the position of this peak of the frequency of the sound wave being attenuated suggests that in $YBa_2Cu_3O_{6+x}$ a phase transition also takes place at $T \approx 240$ K. Calorimetric measurements carried out on non-stoichiometric $YBa_2Cu_3O_{6+x}$ specimens with a high oxygen content confirm this conclusion.[20] All this provides a weighty basis for assuming that the phase transition at $T \approx 240$ K is similar to the transition at $T \approx 1000$ K, due to redistribution of oxygen on the sites of the CuI–O4 basal plane, as a result of which the mode of its ordering in the crystal is changed. As will be explained below, this suggestion imposes quite definite limitations on the choice of the parameters V_0 and V_1 of the interparticle pair interaction (Fig. 1).

We stress in this connection that according to calculations,[15] no changes should occur for large x and $T \approx 240$ K in $YBa_2Cu_3O_{6+x}$. The reason for this consists evidently in the unfortunate choice of the ratio V_1/V_0 which is taken[12,14,15] to be equal to -1 and $-2/3$. In actual fact a more realistic relation would seem to be

$$-V_0 \gg V_1. \tag{1}$$

Actually, the attraction V_0 between O^{2-} ions in an O4–CuI–O4 fragment is most likely due to the fact that the two neighboring oxygen ions ensure the most favorable (fourfold planar) coordination for a Cu ion. In other words, it is

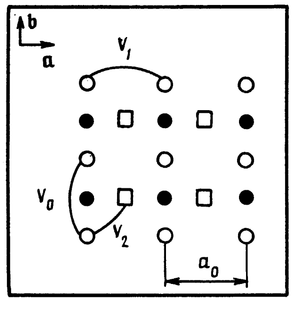

FIG. 1. CuO plane: ●) CuI sites, ○) O4 sites, □) O5 sites.

of a chemical nature and, consequently, should be stronger than the purely electrostatic repulsion V_1. The following considerations also favor relation (1). The interaction V_0, together with V_2 has a decisive role in the high-temperature tetra–ortho transition, as a result of which the O^{2-} ions preferentially align along linear chains formed by O4 sites. As the temperature is lowered O5 sites rapidly empty (see, for example, Ref. 21), so that the repulsion V_2 drops out of play altogether. The phase transition at $T \approx 240$ K, which according to our suggestion is associated with long-range redistribution and ordering of the oxygen in the CuI–O4 plane, should thus occur because of the interplanar interaction V_1 and the size of the latter quantity should determine this. Since the size of V_0 is given by the temperature of the tetra–ortho transition ($T \approx 1000$ K), we again come to the inequality (1). For such a relation between V_0 and V_1 the low-temperature phase transition is possible for all x up to $x \to 1$, as will be seen below.

In the present work the calculation of the T–x diagram for $YBa_2Cu_3O_{6+x}$ is carried out under the following assumptions. The region of the phase diagram corresponding to the orthorhombic crystal structure is considered, when the O5 sites are practically empty, while the oxygen ions are arranged along the chains formed by O4 sites. For O^{2-} ions belonging to one and the same chain, only interactions among O4–CuI–O4 pairs are taken into account; correspondingly, repulsion only occurs between ions of neighboring O4 chains. All the interactions are paired, additive, and independent of the oxygen concentration. In such a formulation the problem comes down to a search for possible means for distribution of O^{2-} ions along the chains referred to above, and also the search for a spatial structure which could form a sequence of such chains in the crystal. The route to solving this problem will consist in the fact that the "intrachain" thermodynamics is taken into account exactly, and for relatively weak interchain interation the mean field approximation is applicable. The following Hamiltonian corresponds to this

$$\begin{aligned} H = \varepsilon_0 \sum_m \sum_{r_m} p(r_m) + V_0 \sum_m \sum_{r_m} p(r_m) p(r_{m+1}) \cdot \\ + {}^1/_2 V_1 \sum_m (x_{m-1} + x_{m+1}) \sum_{r_m} p(r_m), \end{aligned} \tag{2}$$

where ε_0 is the bonding energy of an O^{2-} ion at an O4 site; the projection operator $p(r) = 1$ (0) if there is (is not) an oxygen ion; V_0 ($V_0 < 0$) is the interaction energy of an O4–CuI–O4 pair, V_1 ($V_1 > 0$) is the energy of interaction of an O^{2-} ion with the neighboring chain; m is the O4 chain number, r_m is the site coordinate in the mth chain, x_m the concentration of oxygen ions in the mth chain.

In the mean-field approximation (for the operator of the interaction between chains) the correlation between the mutual position of ions in neighboring chains is not taken into account. In Ref. 15, where the case $V_0 = -V_1$ was considered, these correlations are strong and the use of the mean field approximation would be incorrect. In the limit $-V_0 \gg V_1$ considered by us, these correlations are considerably weaker than intrachain and neglecting them should not lead to appreciable error.

Calculation of the free energy of the system with the energy operator of Eq. (2) is, to a considerable extent, analogous to the corresponding calculation for an isolated chain. Leaving out intermediate calculations, we come to the expression obtained as a result, for the density of the partial free energy density of the system:

$$F(\{x_m\},T)=\frac{1}{M}\sum_{m=1}^{M} f(x_m,T)+\frac{V_1}{M}\sum_{m=1}^{M} x_m x_{m+1} \qquad (3)$$

(m is the total number of chains), where

$$f(z,T)=z(\varepsilon_0+V_0)+2zT\ln\xi-T\ln\left(\frac{1-z-z\xi^2}{1-2z}\right) \qquad (4)$$

is the well known expression for the free energy density of an isolated chain of particles with concentration z and with interaction between nearest neighbors, with

$$\xi(z)=\zeta(z)+[\zeta^2(z)+1]^{1/2}, \qquad (5)$$

where

$$\zeta(z)=\frac{(z-{}^1\!/_2)}{[z(1-z)]^{1/2}}\exp(V_0/2T). \qquad (6)$$

The concentrations of atoms in the chains x_m, appear as order parameters in Eq. (3), satisfying the conservation condition

$$\frac{1}{M}\sum_{m=1}^{M} x_m=x,$$

where x is the macroscopic concentration of oxygen on the O4 sublattice of the basal plane, coinciding with the value of the stoichiometry index in the structural formula $YBa_2Cu_3O_{6+x}$.

Thermodynamic stability of the configuration of the system corresponds to the condition for the equality of the mutual chemical potential of chains

$$\frac{\partial F}{\partial x_m}=\mu, \quad m=1,\ldots,M, \qquad (7)$$

together with the stability condition of the structure determined with the help of Eq. (7), i.e. with the condition for a positive determinant of the matrix Φ, the elements of which have the form

$$\Phi_{m,m'}=\frac{\partial^2 F}{\partial x_m\,\partial x_{m'}}. \qquad (8)$$

Equations (3)–(8) lie at the basis of the further calculations of the present work.

At high temperatures the solution of the system of Eq. (7) is

$$x_m=x \qquad (9)$$

for all m, corresponding to a uniform (O_I) structure of a $YBa_2Cu_3O_{6+x}$ crystal (Fig. 2).

We will study the solution (9) for stability. The elements of the quasidiagonal matrix $\hat{\Phi}$ are in this case [denoting it by $\hat{\Phi}(I)$] equal to

$$\Phi_{m,m}(I)=\varphi_2(x,T),\ \Phi_{m,m+1}(I)=V_1,$$

where

$$\varphi_n(x,T)=\frac{\partial^n f(x,T)}{\partial x^n}.$$

It is easy to convince oneself that the function $\varphi_2\to 0$ (or ∞) for $T\to 0$ (or ∞). It follows from this that for sufficiently high temperature all the eigenvalues of $\hat{\Phi}(I)$ are positive, i.e. the structure O_I is stable. A more exact condition of positive definiteness of the matrix $\hat{\Phi}(I)$ looks like

$$\varphi_2>2V_1. \qquad (10)$$

Actually its eigenvalues

$$\lambda_k=\varphi_2(x,T)+2V_1\cos k,\ 0\leqslant k<2\pi,$$

and the eigenfunctions corresponding to them are

$$B_k(m)=\left(\frac{2}{M}\right)^{1/2}\cos km.$$

For $\varphi_2>2V_1$ all the λ_k are positive. As the temperature is

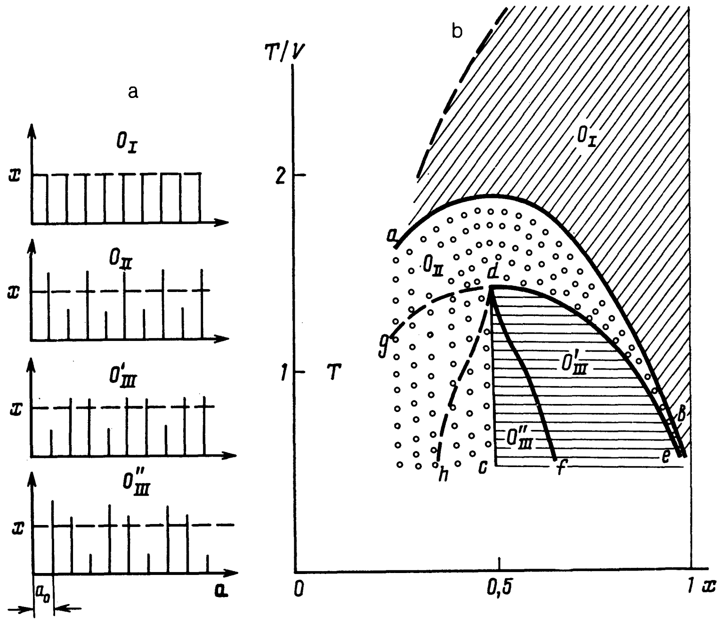

FIG. 2. a) Oxygen concentration distribution for CuI–O4 chains for different structural modifications of the rhombohedral lattice. b) $YBa_2Cu_3O_{6+x}$ phase diagram.

lowered the inequality (10) is reversed and a negative eigenvalue appears. The first negative λ_k's arise in an infinitesimally small vicinity of the point $k = \pi$ and an "alternative wave" corresponds to it

$$B_\pi(m) = \left(\frac{1}{M}\right)^{1/2} (-1)^m. \tag{11}$$

Consequently the $T_1(x)$ curve limited below by the stability temperature region of the O_I structure, is determined by the equation

$$\varphi_2(x, T_1) = 2V_1$$

or, in explicit form,

$$x(1-x)\left[\left(x-\frac{1}{2}\right)^2 + x(1-x)\exp(-V_0/T_1)\right]^{1/2} = T_1/4V_1. \tag{12}$$

It is not difficult to establish the structure of the O_II phase arising at $T < T_1$. It is determined by the "channel" for the collapse of the O_I phase, given by Eq. (11). It follows from Eq. (11) that the state O_II corresponds to successive alternating chains with larger and smaller oxygen concentrations relative to x (see Fig. 2). The elementary cell parameter is then doubled in the **a** direction. We will consider this case in more detail.

We will denote by $x + \delta$ and $x - \delta$ the oxygen concentration in neighboring chains (δ characterizes the depth of the alternation). Then the system of Eqs. (7) leads to the following equation for δ:

$$\ln[\xi(x+\delta)/\xi(x-\delta)] = 2V_1\delta/T. \tag{13}$$

For $T > T_1$ Eq. (13) has a unique solution $\delta = 0$ which corresponds to the O_I structure. For $T < T_1$ another two symmetric ($\pm\delta$) solutions are added to it, which differ from zero. The latter correspond to stable structures if the following equation is satisfied

$$\varphi_2(x+\delta)\varphi_2(x-\delta) > 4V_1^2.$$

Analysis shows that this inequality is satisfied, i.e. the O_II structure is stable if $T < T_1$ (then the solution $\delta = 0$ becomes unstable). In this way, the $T_1(x)$ curve is the second order phase transition line $O_\mathrm{I} \rightleftarrows O_\mathrm{II}$ (curve *a–b* in Fig. 2, b).

Near the phase boundary the order parameter, according to the Landau theory

$$\delta = \pm c(T_1 - T)^{1/2},$$

where

$$c = \left(6\frac{\partial\varphi_2}{\partial T}\Big/\varphi_4\right)^{1/2}\Bigg|_{T=T_1}.$$

The difference between the $T_1(x)$ boundary curve and the corresponding interphase boundary obtained by Zubkus *et al.*[15] consists of the fact that the phase transition $O_\mathrm{I} \to O_\mathrm{II}$ according to Wille *et al.*[12] takes place for all x up to $x = 1$.

It is important to note that besides a simple alternating structure with double elementary cell dimensions of the crystal, Eq. (7) also enables other means of ordering of the oxygen chains along the CuI–O4 basal plane to be determined.

In the present work we limit ourselves to seeking a structure with three-fold period in the **a** direction (O_III phase). Such a situation corresponds to a pattern repeating along the **a** axis, consisting of three consecutive chains with concentrations respectively equal to x_1, x_2, x_3 with $x_1 + x_2 + x_3 = 3x$. In this case Eq. (7) can only be solved by calling on numerical methods. We shall give the main results. It turned out that there are two stable structures with a period equal to $3a_0$: $x_1 = x_3 \neq x_2$ (O'_III phase) and $x_1 > x_2 > x_3$ (O''_III phase) (see Fig. 2, a). The regions corresponding to them is shown in Fig. 2, b. The maximum temperature for stabilization of the O_III phase corresponds to the concentration $x = 1/2$ and is determined from the equation (point *d* in Fig. 2, b)

$$\exp(-V_0/2T_2^*) = 4T_2^*/V_1.$$

In the region of point *d* the curve *g–d–e*, which is the upper limit of stability of the O_III phase, is of the form of an inverted parabola

$$\alpha(T_2^* - T) = (x - 1/2)^2,$$

where

$$\alpha = \frac{16(2T_2^* - V_0)}{3(48T_2^{*2} - V_1^2)}.$$

The *d–f* boundary separates the stability regions of the structures O'_III and O''_III; near the point *d* the curve *d–f* is described by the equation

$$x - \frac{1}{2} = [\varphi_5(1/2, T_2^*)/30\varphi_3(1/2, T_1^*)][3/4\,\alpha(T_2^* - T)]^{1/2},$$

The O_III phase, however, is only thermodynamically stable inside the shaded segment *c–d–e* in Fig. 2, b, where $\mu(O_\mathrm{III}) < \mu(O_\mathrm{II})$, and segregation of the phases O_II and O_III does not take place. Within the segment *g–d–c*, on the contrary, $\mu(O_\mathrm{III}) > \mu(O_\mathrm{II})$, i.e. this part is a region of metastability of the O_III phase. Thus, the boundary *c–d–e* is the equilibrium curve of the phases O_II and O_III and corresponds to first order phase transitions. On this boundary the O_III phase arises with finite modulation amplitude of the oxygen chain concentrations along the **a** axis. Then, near the point *d* on the *d–e* boundary

$$x_1 - x \approx 1/2(x - 1/2) \equiv 1/2[\alpha(T_2^* - T)]^{1/2},$$

$$x_3 = x_1, \quad x_2 = 3x - 2x_1,$$

and on the line *d–c*

$$x_1 = 1/2 + 3/2[\alpha(T_2^* - T)]^{1/2},$$

$$x_3 = 1/2 - 3/2[\alpha(T_2^* - T)]^{1/2}, \quad x_2 = 1/2.$$

As regards the curve *d–f*, it is the line of second order phase transitions. The symmetry element, lost in the $O'_\mathrm{III} \to O''_\mathrm{III}$ transition, is the (100) symmetry plane which passes through a chain with concentration x_2. The point *d* is correspondingly the critical point of the phase diagram.

We note that the O'_III phase is reminiscent in its structure of one of the Magneli phases mentioned by Khachaturyan and Morris.[13] However, there is an appreciable difference, which consists in the chains being completely filled with oxygen. There is not then[13] a corresponding analog of the O''_III phase.

It is easy to accept that Eqs. (7) do not give solutions

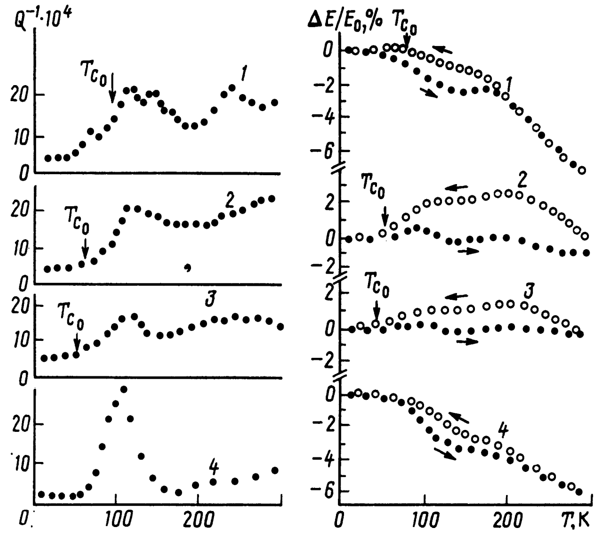

FIG. 3. Temperature dependences of Young's modulus (E) and acoustic losses (Q^{-1}) for specimens of $YBa_2Cu_3O_{6+x}$ with different oxygen contents: 1) $x = 0.9$, 2) 0.68, 3) 0.55, 4) 0.24.

corresponding to stable structures with period $4a_0$. It can also be shown [using the transition to the continuum limit in Eq. (7)] that these equations also do not have stable substructures of high order, taking account only of the interaction between neighboring chains. For this reason it can be suggested that substructures with a period higher than $3a_0$ are absent in the model considered.

DISCUSSION OF RESULTS

An important consequence of the T–x diagram obtained in the present work is the possible existence of both first and second order phase transitions between structural modifications of orthorhombic symmetry in the temperature region $T \ll 1000$ K and for large x.

It is natural to associate the experimentally observed peak in acoustic absorption at $T \approx 240$ K for specimens with high oxygen content with a second order phase transition which corresponds to one of the points of the a–b curve of the diagram shown in Fig. 2, b. As can be seen from the diagram, as the oxygen content changes, the temperature of the phase transition should change; besides that, in the immediate vicinity of this transition at slightly lower temperature, another phase transition occurs, but now of first order (curve d–e in Fig. 2, b). A number of experimental results which we have obtained can, at least qualitatively, be explained on the basis of such a picture.

The results of measuring the temperature dependences of internal friction Q^{-1} (acoustic losses) and also of Young's modulus for ceramic $YBa_2Cu_3O_{6+x}$ specimens are shown in Fig. 3 for different oxygen content (the measurements were made by the method of a compound vibrator made up of specimens prepared by a cryochemical technique, the method for fixing the oxygen was by quenching in liquid nitrogen; the specimens and method were the same as described before.[1,2]

As can be seen from Fig. 3, while for a specimen with high oxygen content ($x = 0.9$) there is a maximum in the acoustic losses at $T \approx 240$ K, the effect of temperature hysteresis of the elastic modulus is observed at lower temperature $T \lesssim 200$ K, which evidently is a manifestation of first-order phase transitions occurring in that specimen. [We first described[1] the appearance of temperature hysteresis on the $E(T)$ curve for specimens with various oxygen contents, now confirmed by the investigations of a whole array of authors (see, for example, Refs. 22–25).] It can also be seen that as the oxygen content decreases, the temperature of the start of hysteresis moves into the region of higher temperatures, which qualitatively agrees with the behavior of the e–d curve in the phase diagram. For example, at $x = 0.68$ the temperature for the start of the effect shifts to $T \gtrsim 300$ K. As regards the peak in acoustic losses at $T \approx 240$ K, its position does not remain unchanged. On lowering the oxygen content to the value $x = 0.68$ this peak is not realized within the limits of 300 K, only the trend of the $Q^{-1}(T)$ curve in the direction of increased losses is seen. According to the phase diagram (Fig. 2, b curve a–b) this peak, associated with a second order phase transition, should in fact occur at $T > 300$ K under conditions for the start of hysteresis (i.e. a first-order phases transition) at $T \approx 300$ K.

It is interesting to note that experiment indicates the existence of correlation between the magnitude of the acoustic loss peak and the amplitude of the temperature hysteresis

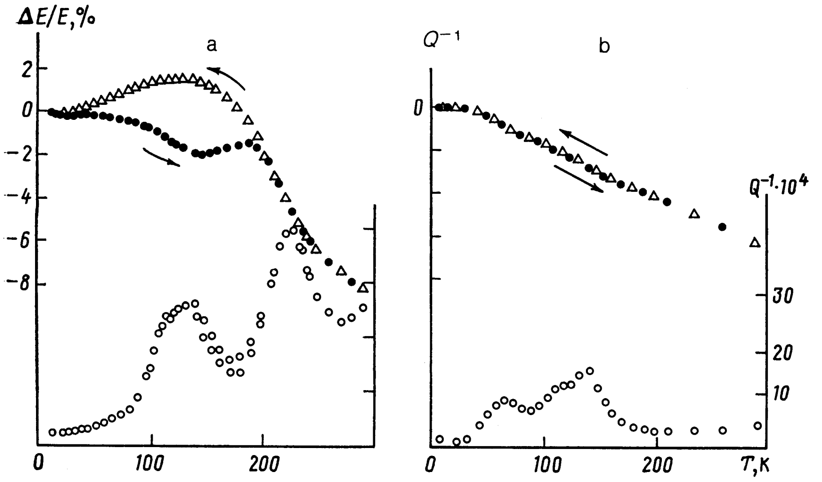

FIG. 4. Temperature dependences of Young's modulus (E) and acoustic losses (Q^{-1}) for a) large-grained and b) ultra-small-grained specimens of $YBa_2Cu_3O_{6+x}$.

of the elastic modulus for specimens with $x \approx 1$. It can be seen from Fig. 4 that in the specimens with the maximum peak on the $Q^{-1}(T)$ curve at $T \approx 240$ K, the effect of temperature hysteresis of $E(T)$ for $T < 240$ K is most clearly shown: if there is no anomaly in the $Q^{-1}(T)$ dependence at 240 K for a specimen, then temperature hysteresis is not observed in $E(T)$.

The absence of the effect considered in some specimens is evidently associated with the influence of dispersion of the grains and internal strains on the properties of HTSC's (Refs. 1, 22). This complicated question is the subject of our further investigation and is not discussed in the present work. The acoustic loss peaks at temperatures $T \sim 60$, ~ 110, ~ 140 K, are of a relaxation nature (their positions depend on the measuring frequency[18,19]) and are also not discussed in the present work.

Earlier,[1] when an explanation was first proposed for the temperature hysteresis effect as a manifestation of first-order phase transitions, the possibility was pointed out of the realization of such phase transitions in local sections, for example near twin boundaries, where the transition of micro-amounts of material of the tetragonal and orthorhombic phases is postulated. The existence of traces of the relaxation peak of acoustic losses at $T \sim 110$ K characteristic of the tetragonal phase, in specimens with large oxygen content, including $x = 0.94$, is evidence in favor of such an explanation. However, the following difficulty then arises: the amplitude of the temperature hysteresis in the $E(T)$ dependence is frequently too high to explain its local variations in the specimen. The first-order phase transition found in the present work in the region of high x enables us to remove this difficulty, since these transitions, unlike local, take place over the whole volume inside a domain.

We note the following in conclusion. The theory expounded above refers to a uniform and infinite medium. In ceramic specimens, however, internal strains arise in their preparation process, which shift to one or other side of the interphase boundary on the T–x diagrams corresponding to different sections of the specimen, which leads to a spread in its local properties. It is just this spread which could explain the extended nature of the hysteresis in the $E(T)$ dependence (Figs. 3, 4). Further, the opinion was confirmed that the manner of the distribution of oxygen along the chains of the CuI–O4 basal plane is an appreciable influence on the superconducting properties of HTSC's. In this case the existence of the spread indicated above would automatically lead to a spatial nonuniformity in the superconducting properties of a specimen. A more detailed analysis of this question could be helpful for resolving this problem, which is being discussed at present.

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