# Anomalously Large Oxygen-Ordering Contribution to the Thermal Expansion of Untwinned $YBa_2Cu_3O_{6.95}$ Single Crystals: A Glasslike Transition near Room Temperature

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We present high-resolution thermal expansion data from 5–500 K of untwinned $YBa_2Cu_3O_x$ (Y123) single crystals for $x \sim 6.95$ and $x = 7.0$. Large contributions to the thermal expansivities due to O ordering are found for $x \sim 6.95$, which disappear below a kinetic glasslike transition near 280 K. The kinetics at this glass transition is governed by an energy barrier of $0.98 \pm 0.07$ eV, in very good agreement with other O-ordering studies. Using thermodynamic arguments, we show that O ordering in the Y123 system is particularly sensitive to uniaxial stress along the chain axis and that the lack of well-ordered chains in Nd123 and La123 is most likely a consequence of a chemical-pressure effect.

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The superconducting and normal state properties of $YBa_2Cu_3O_x$ (Y123) depend strongly both on the total oxygen content (O content) $x$ and on the degree of O order in the CuO chain layer, and a great deal of experimental and theoretical effort has gone into studying both the different types of O-ordered structures and their correlation with superconducting properties [1–23]. Most of these studies have concentrated on samples with O contents in the range $6.3 < x < 6.7$, probably because superconductivity is particularly sensitive to the degree of O order in this range. The kinetics of O rearrangements occurs via a thermally activated diffusion process with a time constant on the order of hours at room temperature, and many interesting effects have been observed by room-temperature annealing studies [7–13].

There are, however, only a few studies in which O-ordering effects have been reported near the optimal doping level ($6.9 < x < 7.0$), where there are only a few O vacancies and much smaller ordering effects are expected. Nevertheless, resistivity studies of Lavrov *et al.* clearly demonstrated that O ordering occurs even in nearly fully doped ($x \sim 6.95$) samples [14]. Further evidence for O ordering in optimally doped crystals has also been obtained by high-temperature quench experiments of Erb *et al.*, in which it was clearly shown that O vacancy clusters form in slowly cooled crystals and that these clusters form strong flux-pinning centers, which are responsible for the "fish-tail" effect [16].

In this Letter we present a thermodynamic and kinetic study of O-ordering processes in near optimally doped ($x \sim 6.95$) $YBa_2Cu_3O_x$ (Y123) untwinned single crystals using high-resolution thermal expansion measurements. Surprisingly large contributions to the linear thermal expansion coefficients (expansivities) from O ordering are observed. These are, as expected, absent in the fully oxygenated ($x = 7.0$) state. The large anomalies imply that O ordering is highly sensitive to slight dimensional changes of the crystal lattice. The largest contribution occurs along the chain axis ($b$ axis), from which the peculiar result, that compressing the chain axis increases the degree of O order, can be inferred. Our results clearly show that the lack of well-ordered chains in Nd123 and La123 [17] is a consequence mainly of the larger (in comparison to Y123) unit cell.

Our investigations have been performed on Y123 single crystals grown by a pulling technique, detwinned at a uniaxial pressure of 10 MPa, and oxygenated at 490 °C [24]. This procedure results in a slightly overdoped sample with an O content $x$ of approximately 6.95. In order to get to the fully oxygenated state with $x = 7.0$, the crystals were annealed at 376 bar O pressure and 400 °C for 140 h. The same crystal, with linear dimensions of $6 \times 3 \times 2$ mm$^3$ for the different orthorhombic axes $a$, $b$, and $c$, respectively, as used in a previous thermal expansion investigation [25], was used presently. The thermal expansion was measured with two different high-resolution capacitance dilatometers in the range 5–300 K and 150–500 K, respectively, using constant heating and cooling rates between 2.5 and 20 mK/s. Data points were taken every 100 mK. The linear thermal expansivities $\alpha(T) = \frac{1}{L}\frac{dL}{dT}$ were obtained by point-to-point differentiation and subsequent averaging over 5 (5–300 K) or 50 (150–500 K) points.

In Fig. 1 we present $\alpha(T)$ of Y123 along the three orthorhombic axes in the temperature range 5–500 K for two different $x$ values [$x \sim 6.95$ (solid line) and $x = 7.0$ (dashed line)]. In addition to the well-studied superconducting anomalies at $T_c$ [25–27], a quite large and broad $\alpha(T)$ anomaly is observed for the $x \sim 6.95$ sample near room temperature, or more precisely at $T_g = 280$ K, along each of the axes. No comparable effect is seen for $x = 7.0$, and in the following we show that this anomaly results from a kinetic glasslike transition due to O ordering.

The shape of the "280 K" anomaly (width [28] and hysteresis for heating and cooling curves) is typical for

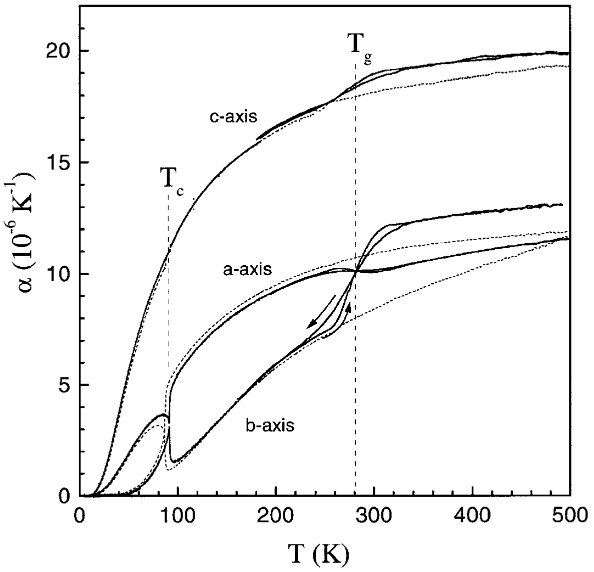

FIG. 1. Expansivity versus temperature of $YBa_2Cu_3O_x$ for the $a$, $b$, and $c$ axes for $x \sim 6.95$ (solid lines) and $x = 7.0$ (dashed lines). In addition to the superconducting phase transition at $T_c$, a glasslike transition can be observed at $T_g$ in the data with $x \sim 6.95$. The arrows indicate heating and cooling cycles.

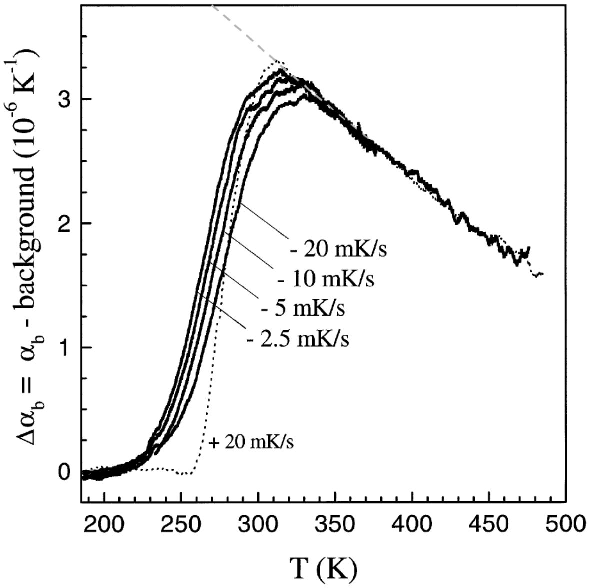

FIG. 2. O-ordering contribution to $\alpha_b(T)$ of $YBa_2Cu_3O_{6.95}$ for different cooling rates (solid lines) and heating with 20 mK/s (dotted line) after cooling with identical rate. The dashed line represents $\Delta\alpha_b^{\mathrm{equil}}$ (see text).

kinetic glass transitions [29–31]. We note that glasslike transitions may also occur in "equilibrium," i.e., not supercooled, states [30,31], and this appears to be the present case. A comparison between the $x \sim 6.95$ and $x = 7.0$ data sets clearly indicates that, as expected [29–31], there are additional contributions ($\Delta\alpha$) to the expansivities above $T_g$, which are absent below $T_g$. The contribution above $T_g$ is positive for the $b$ and $c$ axes and negative for the $a$ axis [32] (see Fig. 1). The largest effect is found for the $b$ axis, for which we have also examined the expansivity as a function of cooling rate for $-2.5$, $-5$, $-10$, and $-20$ mK/s. As seen in Fig. 2, the glass transition shifts to higher temperatures with increasing cooling rates, which clearly indicates the kinetic nature of the transition. Here we have subtracted a background, which was constructed by shifting the data of the $b$ axis for $x = 7$ by a small value, from the original data. In order to extract a well-defined $T_g$ from these broad transitions, we have normalized the data in Fig. 2 by the equilibrium expansivity $\Delta\alpha_b^{\mathrm{equil}}$ (dashed line). Below $T_g$, $\Delta\alpha_b^{\mathrm{equil}}$ is obtained by an extrapolation of the high-temperature data to lower temperatures. In Fig. 3 these normalized curves are plotted versus $-T^{-1}$ in order to show that the glass transition shifts in temperature, while the shape of the glass transition does not change. $T_g$ values can now easily be extracted from Fig. 3 as the midpoints of the transitions, and these are shown in an Arrhenius plot (see the inset in Fig. 3). The data show a good linear dependence, indicative of a thermally activated relaxation time [29–31]

$$\tau(T) = \nu_0^{-1} e^{E_a/k_B T} \tag{1}$$

with an activation energy $E_a = 0.98 \pm 0.07$ eV. The relaxation time $\tau$ at $T_g$,

$$\tau(T_g) = \frac{k_B T_g}{E_a} \frac{T_g}{|r|}, \tag{2}$$

can be directly related to the cooling rate $r$ in our experiment [33], yielding the prefactor $\nu_0 = 1 \times 10^{15}$ Hz in Eq. (1). Our value for the activation energy $E_a$, which is physically related to the barrier for O hopping, is in very good agreement with those found by other kinetic studies of O ordering [5,8,15,34]. This and the fact that the glass transition vanishes for $x = 7$ provides clear evidence that the expansivity anomalies in the $x \sim 6.95$ sample result from the freezing of O-ordering processes. This ordering occurs on a "local" scale, as indicated by the short extrapolated diffusion lengths using the experimental diffusion constants [34] and our relaxation time $\tau(280\text{ K}) = 350$ s. We stress that we see no indications for the so-called "240 K phase transition," which has also been discussed in connection with O ordering [35]. In the following, we analyze the thermodynamics of the O ordering above $T_g$, where thermal equilibrium is guaranteed.

The additional contribution to the expansivity $\Delta\alpha$ above $T_g$ (see Fig. 2) is a direct measure of the uniaxial pressure (stress) dependence of the degree of O order at constant temperature [36]

$$\Delta\alpha_i = -\frac{1}{V_{\mathrm{mol}}} \frac{\partial S_{\mathrm{oxygen}}}{\partial p_i}\bigg|_T \qquad (i = a, b, c). \tag{3}$$

Here $S_{\mathrm{oxygen}}$ is the molar entropy associated with O disorder and $V_{\mathrm{mol}}$ is the molar volume. Inserting the measured $\Delta\alpha$ values at 340 K ($\Delta\alpha_a = -5 \times 10^{-7}\ \mathrm{K}^{-1}$,

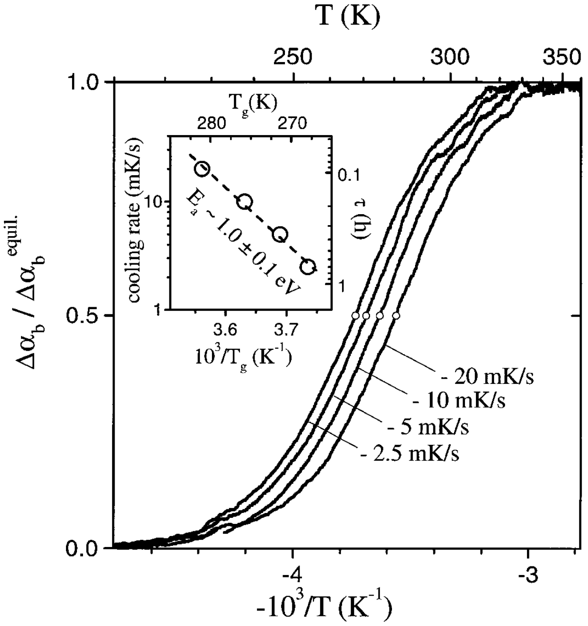

FIG. 3. Normalized plot of $\Delta\alpha_b(T)$ versus $-T^{-1}$ for $x \sim 6.95$. The inset shows an Arrhenius plot of the cooling rate and relaxation time versus $T_g^{-1}$ (see text for details).

$\Delta\alpha_b = 30 \times 10^{-7}\ \mathrm{K}^{-1}$, $\Delta\alpha_c = 8 \times 10^{-7}\ \mathrm{K}^{-1}$) into Eq. (3), we obtain $dS_{\mathrm{oxygen}}/dp_a = 56$ mJ/(mol K GPa), $dS_{\mathrm{oxygen}}/dp_b = -311$ mJ/(mol K GPa), and $dS_{\mathrm{oxygen}}/dp_c = -85$ mJ/(mol K GPa). This shows that uniaxial pressure (stress) along the $a$ axis decreases the O order, whereas uniaxial pressure along the $b$ and $c$ axes increases the O order. Hydrostatic pressure is expected to increase the O order since $dS_{\mathrm{oxygen}}/dp_{\mathrm{hyd}} = \sum dS_{\mathrm{oxygen}}/dp_i = -0.34$ J/(mol K GPa). We can also calculate the change of $S_{\mathrm{oxygen}}$ resulting from volume changes

$$\frac{\Delta S_{\mathrm{oxygen}}}{\Delta V_{\mathrm{mol}}/V_{\mathrm{mol}}} = B\,\Delta\beta\,V_{\mathrm{mol}} = \frac{0.34\ \mathrm{J/(mol\,K)}}{\%\ \mathrm{volume\ change}}, \quad (4)$$

using the bulk modulus $B = 100$ GPa [37] and the O-ordering contribution to the volume expansivity $\Delta\beta$. In order to get a feeling for the magnitude of these pressure (volume) effects, it is instructive to calculate the maximum entropy difference $\Delta S_{\mathrm{oxygen}}^{\mathrm{max}}$ between totally ordered and totally disordered states. For $x = 6.95$ (5% O vacancies) and assuming that the disorder is limited to the disorder in the chains (no O-5 site occupations), $\Delta S_{\mathrm{oxygen}}^{\mathrm{max}}$ can be easily calculated using elementary statistical mechanics to equal 1.65 J/(mol K) [38]. Thus, a relatively small (1%) volume increase (decrease) will result in a quite large (20% of $\Delta S_{\mathrm{oxygen}}^{\mathrm{max}}$) increase (decrease) of $S_{\mathrm{oxygen}}$. This result, which is a direct thermodynamic consequence of our data, provides a simple explanation for the different degrees of O order observed in $R$123 ($R$ = rare-earth) compounds [17]. In $R$123 compounds with a larger (smaller) unit cell (in comparison to Y123) the degree of O order should be much lower (much higher) than in Y123. Nd123, for example, has a unit cell which is about 2.6% larger than that of Y123 [39] and should therefore have an entropy, which is about 0.88 J/(mol K) larger than in Y123—this entropy difference is about 50% of $\Delta S_{\mathrm{oxygen}}^{\mathrm{max}}$ and suggests that Nd123 is nearly fully disordered, in agreement with experiment [17]. Also, the failure to detect any glass transition in Nd123 with $x \sim 6.95$ up to 500 K using dilatometry [18], which implies that $dS/dV = 0$ [see Eq. (4)], suggests that $S_{\mathrm{oxygen}}$ is at its maximum value. Yb123, on the other hand, has a smaller unit cell and is expected to have a higher degree of chain order. Our results suggest that the difference between the degree of O ordering in the $R$123 can be explained by a simple chemical-pressure effect.

Oxygen ordering should also be observable in the specific heat $C_p$, but, unfortunately, even high-resolution measurements have not detected this anomaly [40]. These specific heat data, however, provide an upper limit of about 2 J/(mol K) for this contribution at 300 K. It is instructive to compare this value with the anomaly in

$$C_p - C_V = TV_{\mathrm{mol}}B\beta^2, \quad (5)$$

$\Delta(C_p - C_V)$, which can be directly calculated from the temperature dependence of $\beta$. Just above $T_g$, $\Delta(C_p - C_V) = 0.8$ J/(mol K), which is 40% of the maximally estimated $C_p$ contribution (see above). This indicates that, in addition to the usual increase in entropy due to increasing temperature, the volume change due to the thermal expansion plays a major, if not dominating, role in the increase of entropy with increasing temperature; this is because the $dS/dV$ term is so large. Another way to quantify the strong volume dependence is through a partial Grüneisen parameter for O ordering:

$$\gamma_{\mathrm{Grüneisen}}^{\mathrm{O\ ordering}} = \frac{\Delta\beta\,V_{\mathrm{mol}}B}{\Delta C_p}. \quad (6)$$

Inserting the maximum estimate for the $C_p$ contribution (see above) just above $T_g$ into Eq. (6) yields a lower limit for $\gamma_{\mathrm{Grüneisen}}$ (>17). An upper limit ($\gamma_{\mathrm{Grüneisen}} <$ 43), on the other hand, is obtained by realizing that $\Delta C_v$ must be greater than or equal to zero, from which a lower limit of $\Delta C_p \geq 0.8$ J/(mol K) can be inferred [see Eq. (5)]. Such large values of $\gamma_{\mathrm{Grüneisen}}$ clearly document the enormous pressure/volume dependence of the O-ordering effects in Y123.

So far we have not discussed either the spatial arrangements or the microscopic origin of these ordering processes. From optical measurements it is clear that the mean O-chain length is growing as one lowers the temperature [19]. This is also compatible with the hole transfer from chains to planes, which is expected as the chains increase in length [20], observed by Lavrov *et al.* [14], as well as with the formation of O clusters [16]. Theoretically, O ordering has been modeled using the asymmetric-next-nearest-neighbor-interaction (ASYNNNI) model, in which several phenomenological parameters ($V1 > V2 > V3 > \cdots$) are introduced to describe the O interactions in the basal plane [21–23]. We note that we do not observe the thermodynamic phase-separation line (ortho-I ↔ ortho-I + ortho-III) predicted by this model [22] in our experimental temperature window ($280 < T < 500$ K). The parameter $V2 \approx 2000$ K determines the length of the chains in this model. A recent theoretical study has argued that a single $V2$ parameter is too simple and that this interaction depends on chain length as well as on $x$ [41]. Our results show that $V2$ depends also strongly on the size of all lattice parameters, which demonstrates the complexity of this interaction. We should point out that this cannot be understood in terms of a simple steric effect involving just the $b$-axis parameter, since $V2$ also depends on the size of the other axes, and any *ab initio* calculations of $V2$ will most likely have to include the electronic structure of the whole unit cell, including effects such as charge transfer, etc. [42].

In conclusion, our thermal expansion data of untwinned single crystals clearly reveal the kinetics and, for the first time, also the thermodynamics of O-ordering effects in $YBa_2Cu_3O_{6.95}$. These ordering effects manifest themselves in terms of a kinetic glasslike transition near room temperature. The large size of the glass-transition anomalies along all axes is directly correlated with the extreme dependence of the degree of O order with the lattice parameters, and this provides a natural explanation of the different O order, for example, in Nd123 and La123 in terms of a simple chemical-pressure effect. Studies of O ordering in $R$123 compounds using high pressure or strain induced by lattice mismatch in thin films should provide further valuable information [43]. Theoretical modeling of the O ordering via lattice gas models, such as the ASYNNNI model, should incorporate this new result for a more quantitative comparison with experiments.

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