Thermal hysteresis of the elastic modulus and low-temperature local order-disorder phase transitions in $YBa_2Cu_3O_x$ superconductors

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A thermal hysteresis of the Young's modulus has been detected in the $YBa_2Cu_3O_x$ compounds with the oxygen concentration in the range $6.24 \leqslant X \leqslant 6.9$. This effect is interpreted on the basis of a model which postulates the presence of local first-order order-disorder phase transitions.

The study of the temperature dependence of the elastic moduli is an effective method of obtaining information on the electron-lattice interaction and on the crystal structure of the compounds being studied.

Because of the unusual sensitivity of the elastic properties of the high-T_c superconductors $YBa_2Cu_3O_x$ to the oxygen content, we thought it worthwhile to study their elastic characteristics in the range of variation of x in which the compound undergoes a transition from the superconducting orthorhombic state to the nonsuperconducting tetragonal phase.

We studied the temperature dependence of Young's modulus, $E(T)$, in the temperature interval 4.2–300 K of the ceramic samples of the composition $YBa_2Cu_3O_x$ with the oxygen concentration in the range $6.24 \leqslant x \leqslant 6.9$. The values of Young's modulus were calculated from the measurements of the longitudinal velocity of sound by the composite-vibrator method at a frequency of 170 kHz.$^{1)}$ To eliminate the effect of randon impurities, we used for the measurements principally one sample (sample 1) which was synthesized using cryochemical technology.[1] Different oxygen concentrations in the sample were attained by sequentially annealing it at temperatures of 900, 700, 600, 500, and 400 °C and then quenching it in liquid nitrogen. To measure the functional dependence $E(T)$, we used a specially prepared superfine-grained sample (sample 2) (grain size $\gtrsim 100$ Å) with an orthorhombic structure devoid of twinning boundaries.

The parameter x was determined within ± 0.03 by oxidation-reduction titration. The phase composition was monitored by x-ray diffraction method.

Figure 1 is a plot of the $E(T)$ curves for the compounds $YBa_2Cu_3O_x$ with different values of x. In all cases we observed a temperature-induced hysteresis of the elastic modulus, whose behavior and magnitude differed for samples with different oxygen concentrations. These quantities are, however, virtually independent of the cooling and heating rates of the sample (the rates were varied from 1° to 7° C/min).

The ac measurements of the magnetic susceptibility (in the absence of a static magnetic field and in ~20-Oe fields) showed that T_c and the size of the superconduct-

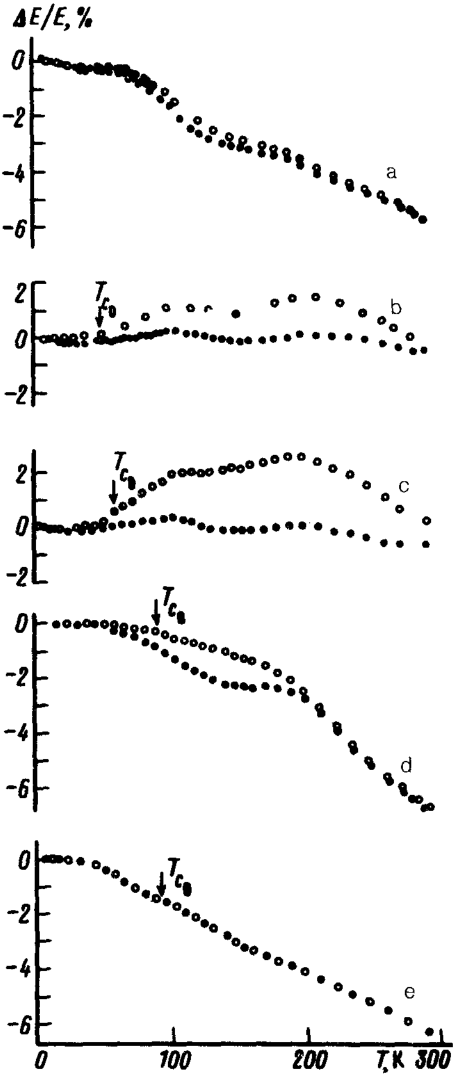

FIG. 1. Temperature dependence of the elastic modulus of $YBa_2Cu_3O_x$, where x: a—6.24; b—6.55; c—6.68; d—6.9; e—6.88. ●—Heating; ○—cooling. Sample 1—Curves a–d; sample 2—curve e.

ing phase decrease with decreasing x (Fig. 2). Since the test compounds have, according to the x-ray data, a largely orthorhombic structure (a moderate presence of the tetragonal phase was detected only in a sample with $x = 6.55$), we can assume that the superconducting phase in the crystallites is distributed nonuniformly. In other words, we can assume that the crystallites contain local domains with a disordered arrangement of the oxygen vacancies, characteristic of the tetragonal phase. The fact that these heterophase domains are stable in the crystallites up to room temperature can be attributed to the elastic strain which develops, for example, at the twinning boundaries.

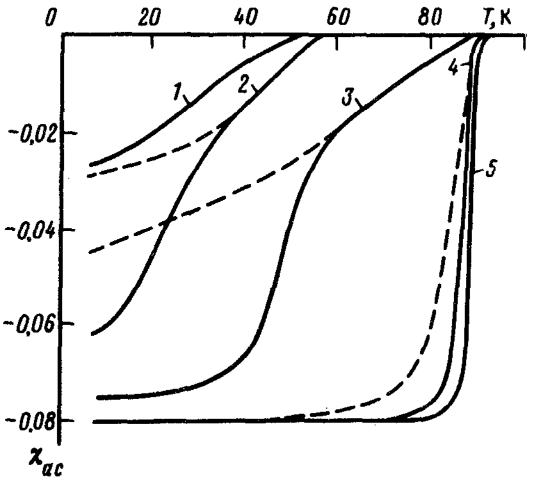

FIG. 2. Temperature dependence of the susceptibility χ_{ac} of $YBa_2Cu_3O_x$ for x: 1—6.55; 2—6.68; 3—6.78; 4—6.9; 5—6.88. Solid curves $H = 0$.

We assume that the detected temperature-dependent hysteresis of Young's modulus stems from the ordering of the oxygen vacancies in the local domains of the crystallites, in which the order-disorder phase transitions occur at temperatures much lower than $T_c \approx 100$ K of the bulk of the crystallites.

We know that in the tetragonal-orthorhombic phase transition changes occur primarily in those atomic layers which contain the Cu1 ions and which have two types of oxygen positions, O4 and O5. A disordered filling of these positions in the tetragonal phase gives way to a Partial or total ordering of the oxygen ions in the O4 positions in the orthorhombic phase. On the basis of this model we find the following expression for the free energy F of the crystal in the mean-field approximation:

$$F(T, \eta) = \frac{B}{2}\eta^2 + \frac{D}{4}\eta^4 - TS(\eta), \tag{1}$$

where T is the temperature, S is the configurational entropy, η is the order parameter of the oxygen ion system in the Cu1-O4-O5 layer, and B and D are coefficients which depend on the oxygen concentration and on the energy of the interaction of the oxygen ions with each other and with the lattice.

The second term on the right side of expression (1) takes into account the local deformation of the cell occurring as a result of the change in the oxygen sublattice. This term is nonvanishing if the interaction of the oxygen ions is nonadditive in the first coordination sphere.

The presence of a term with $D < 0$ in expression (1) accounts for the fact that the function $F(\eta)$ has three minima in a certain temperature interval (which is determined by the ratio of the coefficients B and D), and the order-disorder phase transition becomes a first-order phase transition, which is accompanied by a thermal hysteresis of the order parameter. It is reasonable to expect that E is a function of η, so that the functional dependence $E(T)$ should also exhibit a hysteresis.

The appreciable thermal hysteresis interval observed experimentally can be explained in terms of the proposed model by the scatter in the values of the parameter B in the sample. This scatter also accounts for the difference in the magnitudes of the effect in the samples synthesized by different methods (for comparison see the data of Ref. 2). The concentration dependence of the effect can also be logically deduced from this model.

A total absence of thermal hysteresis in a supersmall-grained sample, in which there are no twinning boundaries (curve e in Fig. 1), confirms the arguments presented above.

We note in conclusion that a sample with an orthorhombic structure and with $T_c = 92$ K, in which thermal hysteresis is not observed, shows no "softening" of the elastic modulus as the temperature is lowered from 300 K to 4.2 K and no structural features at the point T_c, which ordinarily suggest a strong electron-lattice interaction in superconductors.

1)Because of the scattering of rf sound from structural irregularities of the test samples, we had to use low-frequency methods. As a result, we could not obtain reliable results for the single crystals because of their small size.

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[1] A. R. Kaul', I. É. Graboĭ, and Yu. D. Tret'yakov, in: *Superconductivity. The Study of High-T_c Metal-Oxide Superconductors*, I. V. Kurchatov Institute of Atomic Energy, Moscow, 1987, p. 8.

[2] V. Müller, K. De Groot, D. Maurer, Ch. Roth, and K. H. Rieder, Jpn. J. Appl. Phys. **26**, Sup. 26–3, 2139 (1987).

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