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ULTRASONICALLY STIMULATED ORDERING EFFECTS IN THE Y-BA-CU-O SYSTEM

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The effect of ultrasound on the x-ray spectra and electron-positron annihilation in ceramic $YBa_2Cu_3O_{7-x}$ was studied. It is shown on the basis of the x-ray data that the ultrasound leads to an ordering of the oxygen in the basal plane of the unit cell: the order parameter increases from 0.60 to 0.85. There is also a decrease in the defectiveness of the material. The ordering of the anions in the basal plane causes a redistribution of the electron density over the volume of the unit cell. The redistribution of electron density contributes to the changes in the lattice constants.

Key words: Ultrasound, $YBa_2Cu_3O_7$ ceramic, Order parameter

1. INTRODUCTION

Since substantial deviations from oxygen stoichiometry are possible in the Y-Ba-Cu-O system, the first stage of research on this system focused on determining the dependence of structural parameters on the oxygen content (the anion content) in the unit cell. However, it can be concluded from Refs. 1 and 2 that the oxygen index is not the only factor which influences the values of the lattice constants. This assertion is supported in particular by the nonmonotonic changes in the parameters of the electronic structure according to data from electron-positron annihilation [3].

The possibility of various types of structural ordering effects has been discussed in several places [2, 4]. Structural ordering of this sort would be accompanied by a redistribution of the electron density, which might in turn lead to changes in the lattice constants. One example of this ordering was described in Refs. 2, where, in a study by x-ray photoelectron spectroscopy of oxygen (OIS), it was shown experimentally and theoretically that structural changes occur at the O(2) and O(3) sites in connection with a dimerization of oxygen atoms (a grouping of the perovskite type in the CuO_2 plane).

Our approach in the present study was to use several methods to learn about ultrasound affects the oxygen ordering, the distribution of the electron density, and the lattice constants in ceramic $YBa_2Cu_3O_{7-x}$. The measurements methods used in the experiments were time-resolved and angle-resolved electron-positron spectroscopy and x-ray diffraction.

2. EXPERIMENTAL

The ceramic $YBa_2Cu_3O_{7-x}$ test samples had a density ρ=5.5 g/cm^3 and a grain size of 5-20 μm. They were prepared by solid – phases synthesis. The starting materials were powdered Y_2O_3, $BaCO_3$, and CuO. A first annealing was carried out at 850 ^oC in flowing oxygen, with intermediate grinding and mixing. The pressed ceramic was sintered in an oxygen atmosphere at 950 ^oC for 10 h. The samples were cooled at a rate of 200 deg/h to 400 ^oC. After maintaining 3 h at this temperature, the samples were cooled to room temperature with the rate of 50 deg/h.

Ultrasound was applied to the samples by means of piezoelectric transducers made from the ceramic piezoelectric material TsTS-19. The test samples, a platelet with dimensions of 15 × 15 × 2 mm^3, was placed on the transducer. The sample was held in place by an elastic spacer, which doubled as an absorber of the

ultrasound which had propagated from transducer through the sample. Longitudinal ultrasonic waves along the thickness were excited in the transducer at the fundamental resonant frequency of 22 kHz. These waves were coupled into the test sample un the direction perpendicular to the plane of the sample. The ultrasound was applied in a continous regime, at room temperature, under atmospheric conditions. The intensity of the ultrasound which was excited was ~ 5W/cm^2. The warming of the samples did not exceed 5^{o}C. We know that heat treatment of this sort does not lead to residual changes in the parameters of the ceramic. The optimum duration of the ultrasonic processing was 15 min. A further increase in the processing time led no to further changes in the properties of the samples.

The X-ray studies were carried out on DRON-1 (Cu K_α radiation) and ADP-1 (Cu K_β radiation) diffractometers. All the samples consisted of essentially a single phase. The oxygen content was determined from the relation [5] x=7.138 c - 83.275, where c is in angstroms. This content turned out to be close to the stoichiometric value (x≈0). The orthorombic distortion was high: e= (a-b)/(a+b) =0.0165. The lattice constants were determined from a scanning of the 005, 006, 200, 007, 116, 213, 206 and 00.11 reflections. The lattice constants satisfies the relation a=b=c/3.

3. RESULTS AND DISCUSSION

The degree of order of the oxygen in the $YBa_2Cu_3O_{7-x}$ system was found as $\eta = \left[C_{O(5)} - C_{O(4)}\right] / \left[C_{O(4)} + C_{O(5)}\right]$, where $C_{O(4)}$ and $C_{O(5)}$ are the oxygen concentration in the O(4) and O(5) sites in the CuO-1 plane [5]. The quantity η can be calculated from

$$\eta = \frac{(3.1+1.25x)}{(1-x)} \cdot \frac{(r-0.986)}{(r+0.986)}, \qquad (1)$$

where x is the oxygen deficiency index, and r = I_{102}/I_{012}. To determine the intensities of the 102 and 012 reflections, we carried out a triple scanning of the interval 23-27^o (Cu K_β radiation) at steps of 0.01^o. The results of these measurements are shown in Table 1.

Table 1 The lattice parameters of Y $Ba_2Cu_3O_7$ before and after ultrasonication

Sample	a, Å	b, Å	c, Å	x	η
Before ultrasonication	3.822(2)	3.890(2)	11.664(5)	0	0.60
After ultrasonication	3.826 (2)	3.890(2)	11.676(5)	0.07	0.85

The positron lifetime was measured on a standard ORTEC instrument, whose resolution function had a full width at half maximum of 250 ns. The distributions were described by a superposition of several decaying exponentials, convolved with the instrumental resolution function R(t):

$$N(t) = \sum_{j=1}^{im} \int_{-\infty}^{t} R(t_1 - t_0) e^{-(t-t_1)\lambda_j} I_j \lambda_j \, \mathrm{d}t_1 . \qquad (2)$$

Here I_j is the intensity of component j, λ_j is its decay rate, t_0 is the time at which the positron is created, and im is the number of components into which the distribution is decomposed. The distributions in ceramic $YBa_2Cu_3O_{7-x}$ contain two components before and after the ultrasonic processing.

Spectra of the angular correlation of annihilation photons (ACAP spectra) in the $YBa_2Cu_3O_{7-x}$ samples were measured by a spectrometer with a long- slit geometry based on an SEG-S-06 instrument and an AMA-02F-1 analyzer, controlled by a DVK-2M computer. The angular resolution of the spectrometer was 1 mrad for this experiment. The best approximation of ACAP spectra was a superposition of two Gaussians:

$$A(\theta) = A_1(0)\exp(-\theta^2/2\sigma_1^2) + A_2(0)\exp(-\theta^2/2\sigma_2^2), \qquad (3)$$

where $A_1(0)$ and $A_2(0)$ are the intensities of the spectral components at an angle $\theta=0$, and $\sigma_1$and σ_2 are the standard deviations of the wide and narrow Gaussians, respectively. We also determined the contribution of the broad component, S_1/S, where S_1 is the area under the curve of the broad component, and S is the area under the entire ACAP curve. The results of the measurements of the positron-annihilation parameters are listed in Table 2.

Table 2 The positron – annihilation parameters

	τ_1, ns	I_1, %	τ_2, ns	I_2, %	τ_b, ns	σ_1, mrad	σ_1, mrad	S_1/S
Before ultrasonication	0.169	82.7	0.312	17.3	0.183	9.502	4.593	0.089
After ultrasonication	0.172	87.4	0.347	126	0.183	10.83	4.61	0.055
Error	±0.004	±2.6	±0.013	±2.6	±0.005	±0.5	±0.03	

In view of the difference between the depths to which positrons and x rays penetrate into the test material, we compared the experimental data for samples of various thicknesses (2, 1.0 and 0.7 mm). We found no differences in the characteristics which we were studying, so we were able to carry out a comparative analysis of the data from the x-ray and positron spectroscopy.

We see from Table 1 that an ordering of anions occurs in the basal plane of the unit cell of $YBa_2Cu_3O_{7-x}$ after the ultrasonic treatment (the order parameter increases from 0.60 to 0.85). Some of the samples exhibited an increase in η to 1.0. Changes were also observed in the lattice constants.

According to Table 2, the ultrasonic treatment causes a substantial change in the longlived component, τ_2, while having essentially no effect on the short-lived component, τ_1. Note the sharp decrease in the intensity of component τ_2, i.e., I_2.

According to data in the literature [6], the component τ_1 is associated with an annihilation of positrons by valence electrons. The component τ_2 stems from annihilation of positrons "captured" by various structural defects with a relatively low electron density (low in comparison with the defect-free matrix). These structural defects are primarily cation vacancies, phase boundaries, grain boundaries, and twin planes [6,7]. However, in view of the relative contributions of the volume and the surface of the grains to the long-lived component, we conclude that the decrease in I_2 observed after the ultrasonic processing is evidence of a decrease in the defectiveness of the interior of the grains. The observed increase in τ_2 after the ulktrasonic processing may be due to either an increase in the size of the defects (with no change in the size of the defects). The value of τ_1 remains constant, within the experimental errors. The same is true for the positron lifetime τ_b, which is found from the expression

$$\tau_b = (I_1/\tau_1 + I_2/\tau_2)^{-1}. \quad (4)$$

According to Ref. 8, an increase in the oxygen concentration is accompanied by a decrease in the short-lived component τ_1. According to Ref. 7, a decrease in τ_1 is caused by a decrease in the volume of the unit cell, i.e., by an increase in both the volume of the unit cell and the order parameter after the ultrasonic processing), one might suggest that the component τ_1 is insensitive to an increase in the volume of the unit cell acompanied by a simultaneous ordering of the anion sublattice.

The ACAP parameters, which contain differentiated information on different parts of the unit cell, change substantially after the ultrasonic processing (Table 2). If a positron is in a delocalized state, then the positrons are sensitive to changes in the lengths of both the O(4) and O(1) bonds. Let us assume that the narrow ACAP component (σ_2) is a consequence of an annihilation of positrons with 2p and 2s electrons of oxygen ions, since the bond of the Cu $d_{x^2-y^2}$ electrons with the nearest O_4^{2-} anion, with electrons of the 2p and 2s orbitals, is of a delocalized nature. We attribute the broad ACAP component (σ_1) to the annihilation of positrons with d_{z2} bonds of Cu with electrons of bridge oxygen O(1) and Ba-O bonds, since the d_{z2} orbitals are highly localized.

Analyzing the data in Table 2, we note that the standard deviation of the broad component, σ_1, increases after the ultrasonic processing. A similar change in σ_1 has been observed [3] upon a change in oxygen stoichiometry (specifically, an increase in the oxygen concentration) [3].

4. CONCLUSIONS

During ultrasonication of the Y-Ba-Cu-O sample the x-ray measurements reveals a decrease in the oxygen concentration in the unit cell.

From the positron annihilation measurements resulted that the observed increase in σ_1 is the consequence of an ordering of oxygen in the basal plane. The component σ_2, which is directly related to positron annihilation in the basal plane, remains essentially unchanged, but the corresponding contribution increases by 4%.

In summary, the analysis of the set of data presented above shows that the ultrasonic processing leads to an ordering of the anion sublattice of $YBa_2Cu_3O_{7-x}$. The ordering of anions in the basal plane redistributes the electron density over the volume of the unit cell. This redistribution of the electron density contributes to the changes in the lattice constants.

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