# PECULIARITIES IN TEMPERATURE DEPENDENCE OF STRUCTURAL PARAMETERS OF HIGH-$T_c$ 1—2—3 SUPERCONDUCTOR BASED ON SAMARIUM ZERO-MATRIX

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The question about the importance of structural fragments like Cu—O planes and chains for the high-$T_c$ superconductivity (HTSC) phenomenon in 1—2—3 type metal-oxides is certainly one of the most important. To solve this problem it is necessary to further optimize the accuracy of a diffraction measurement to allow a sensitive analysis of separate fragments of the crystal structure of the studied compound. Neutron diffraction offers a unique possibility by help of using the isotope contrast method.

The structural investigations of HTSC ceramics with following chemical composition $^{152.76}Sm_{1.01(2)}\times$ $\times Ba_{1.94(4)}{}^{63}Cu_{3.01(6)}O_{6.9}$ within the temperature range of $63K \leqslant T \leqslant 99K$ and at $T=300$ K were carried out on the high resolution neutron time-of-flight powder diffractometer 'Mini-Sfinks' /1/. The measurements of the temperature dependence of resistance (fig. Inset.) and the magnetic susceptibility of this sample showed the presence of superconducting transition.

To increase the sensitivity of the experiment to resolve better the Ba—Cu—O fragment of the structure we have utilized the isotope contrast method using a mixture of $^{152}Sm$ and $^{154}Sm$ isotopes in the corresponding ratio and the $^{63}Cu$ isotope. The average scattering amplitude of the Sm sublattice has diminished to 0 (zero-matrix composition). The contribution of the Cu-sublattice was also decreased by using the $^{63}Cu$ isotope which has a considerably smaller coherent scattering amplitude than that of the natural isotope mixture. The sensitivity of the experiment for the analysis of the oxygen sublattice was thus further enhanced.

The data of neutron diffraction were processed employing the Rietveld method adopted for the RTOF-version of the profile-refinement program. Corrections for absorption and primary extinction were also introduced. A typical diffraction pattern for this sample (at 300 K) is represented in fig.(1). The difference between observed and calculated profiles is shown below (fig.(2)). The refined atomic positions are summarized in the Table.

| T,K / $\chi^2$ | | 63 / 3.6 | 76 / 3.0 | 83 / 5.0 | 87 / 7.0 | 91 / 5.2 | 99 / 4.0 | 300 / 2.4 |
|---|---|---|---|---|---|---|---|---|
| ATOM | □CCUP. | X<br>y<br>z | X<br>y<br>z | X<br>y<br>z | X<br>y<br>z | X<br>y<br>z | X<br>y<br>z | X<br>y<br>z |
| Sm | 1.0 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| Ba | 1.0 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | | 0.1836(4) | 0.1831(4) | 0.1820(3) | 0.1826(2) | 0.1837(3) | 0.1814(4) | 0,1821(4) |
| Cu1a | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| Cu2q | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.3533(2) | 0.3534(2) | 0.3535(2) | 0.3530(1) | 0.3527(2) | 0.3528(2) | 0.3535(2) |
| O2q | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.1593(3) | 0.1594(3) | 0.1609(2) | 0.1596(2) | 0.1590(2) | 0.1600(3) | 0.1593(3) |
| O2s | 1.0 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.3668(4) | 0.3701(3) | 0.3693(3) | 0.3694(2) | 0.3698(3) | 0.3698(3) | 0.3698(4) |
| O2r | 1.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | | 0.3723(5) | 0.3724(4) | 0.3716(4) | 0.3717(3) | 0.3712(4) | 0.3725(4) | 0.3737(5) |
| O1e | 0.91 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| | | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 | 0.5 |
| | | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 | 0.0 |
| a,Å | | 3.8520(1) | 3.8529(1) | 3.8530(1) | 3.8530(1) | 3.8536(1) | 3.8537(1) | 3.8603(1) |
| b,Å | | 3.8986(2) | 3.8995(2) | 3.8988(1) | 3.8991(1) | 3.8991(1) | 3.8995(1) | 3.9058(2) |
| c,Å | | 11.6879(5) | 11.6915(4) | 11.6912(3) | 11.6914(3) | 11.6940(3) | 11.6930(4) | 11.7245(5) |

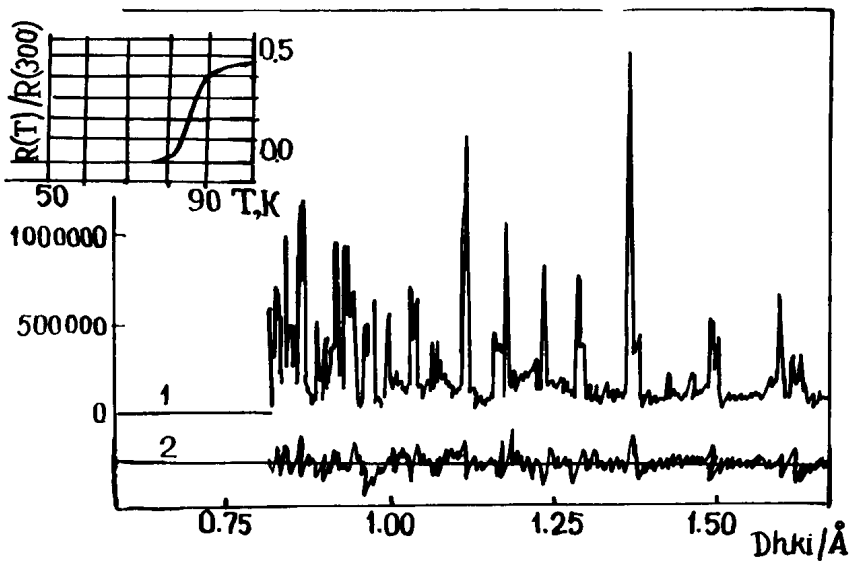


Fig.

The anomalous temperature behaviour of structure parameters (i. e. the atomic positions and Debye-Waller factors) of oxygen and barium ions near and below the superconducting transitions temperature $T_C$ was found. The shifts along the C-direction of the barium and oxygen atoms in 2r and 2s position at $T \cong T_C$ are clearly seen in the Table. Whereas the coordinates of the Cu atoms remain almost independent of temperature.

When the oxygen deficiency decreases, the effective negative charge of the layers containing CuO chains increases. This leads to the creation of holes within the $CuO_2$ layers. Free holes accomplish screening of the excessive negative charge of the $Sm\,2(CuO_2)$ structural element. Furthermore their distribution within the unit cell should be diminished as possible electric dipole moments are directed along the c-axis of dimpled $CuO_2$ and BaO planes. Any fluctuations of these dipole moments have to be responded by hole density redistribution and vice versa.

The structural transformation described above increases the dipole moments of the ionic host and thus enhances the 'dielectric' susceptibility of the matter. This should lead to the enhancement of interelectron coupling and relieve the Cooper pairing.

The opposite situation is also possible, when a change in the free carrier density distribution is connected with a superconducting transition and provokes the charge displacement within the ionic host, i. e. the variation of dipole moments.

**REFERENCE**

1. *Krutov G. A., Kudryashev V. A., Kurbakov A. I. et al.* Preprint LNPI-1543, Leningrad, 1989, 16 p.