MIXED VALENCE STATE IN VARIOUS HIGH T_C SUPERCONDUCTORS

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Different models with structure instabilities are popular now among the theoretical interpretations of high temperature superconductivity mechanism. The mixed valence state is one of such instabilities. The existence of mixed valence charge density can provide the strong binding of charge carries. In connection with the frequency of fluctuation it may lead to the two-pit potential and consequently to the strong anharmonism of thermal oscillations of atoms and anomaly in changing structure parameters. To increase the sensitivity of the experiment to various structure fragments we applied isotopes Sm, Gd, Fe, Cu, Nd, B. The following compounds were prepared: $^{"0"}SmB_6$, $^{154}SmB_6$, $LnN_2Cu_3O_{7-d}$, where Ln= $^{"0"}Sm$, ^{160}Gd, ^{153}Eu, $ReBa_2Cu_{3-x}{}^{57(58)}Fe_xO_{7+d}$, where Re = $^{"0"}Sm$, Y, x = 0.24, Ln_2CuO_4, Ln = ^{144}Nd, $^{"0"}Sm$.

We choose the SmB_6 as the model compound with an element in mixed valence state. The existence of 6% vacancies in B-sublattice was found and temperature dependencies of unit cell parameters were obtained. The latter point out on a change of the average valence of Sm with temperature and this fact demonstrates that the energy splitting can be compared with kT. We obtained thermal tensor values and defined Einstein temperature for Sm-sublattice ($T_E = 120\ K$).

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1) The sample consisted of ~20% 2:2:0:1 - phase ($Tc \sim 10\ K$), ~40% 2:2:1:2-phase ($Tc \sim 90\ K$) and ~40% 2:2:2:3-phase ($Tc \sim 120\ K$).

2) The $K_{\alpha 1}$ - line shift of Sb for the two samples synthesized at the Sb_2O_3 and Sb_2O_5 basis is equal to $\Delta E = 7 \pm 8\ meV$.

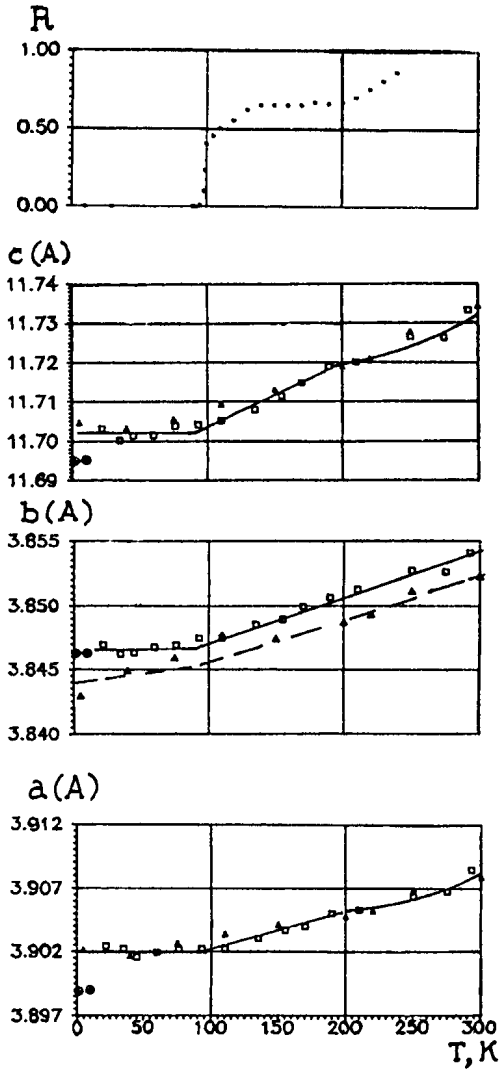

Fig.1.Temperature dependences of unit cell parameters for $SmBa_2Cu_3O_{7-d}$: П — Mini-SFINKS, Δ — D2B, o — DMC

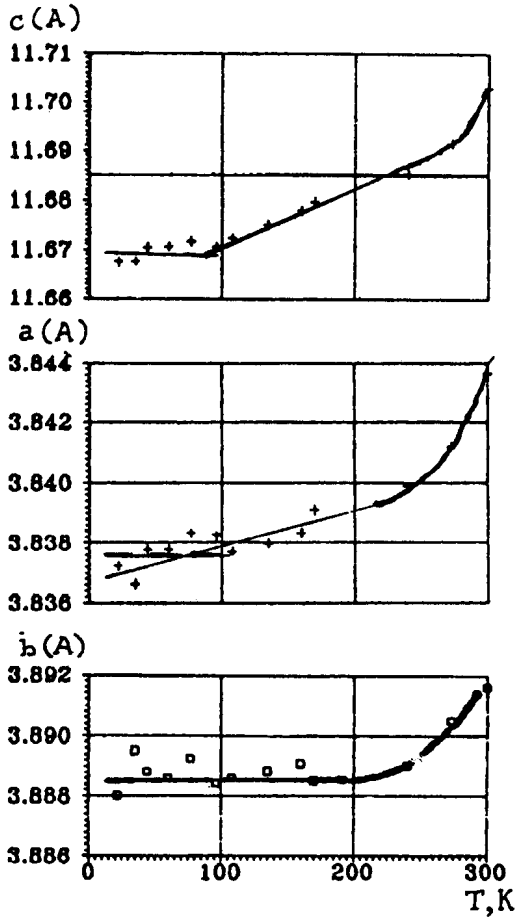

Fig.2. Temperature dependences of unit cell parameters for $GdBa_2Cu_3O_{7-d}$

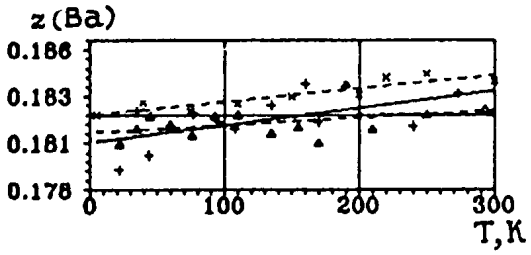

Fig.3. Temperature dependence of Ba z — coodinate for ceramics: + — $GdBa_2Cu_3O_{7-d}$, Δ— $SmBa_2Cu_3O_{7-d}$ (both Mini-SFINKS), x — $SmBa_2Cu_3O_{7-d}$ (D2B)

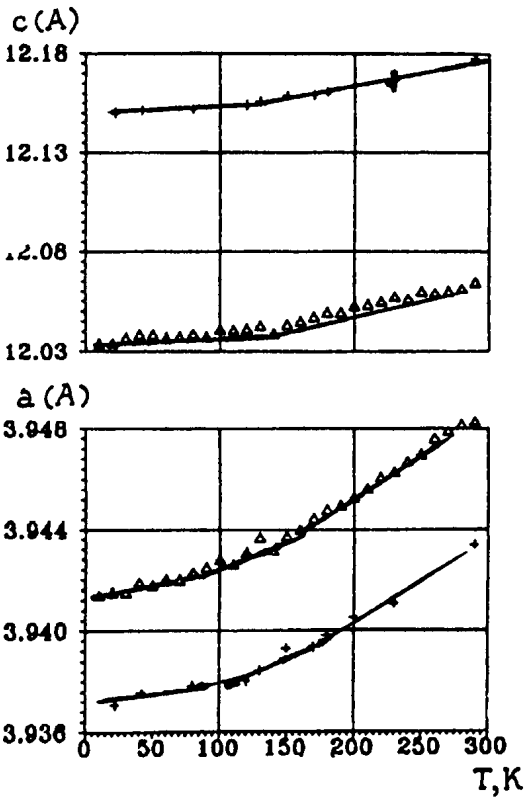

Fig.4. Temperature dependences of unit cell parameters for ceramics: + — Nd_2CuO_{4+d} (Mini — SFINKS), — $Nd_{2-x}Ce_xCuO_{4+d}$ (from [2])

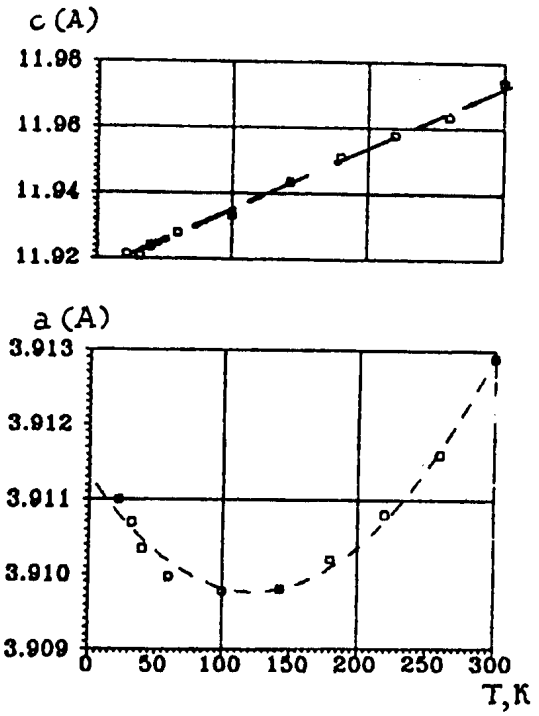

Fig.5. Temperature dependences of unit cell parameters for Sm_2CuO_{4+d}

We studied $^{"0"}$Sm—1—2—3 cermics using three neutron powder diffractometers: Mini-SFINKS, D2B, DMC [1] and ^{160}Gd—1—2—3 on Mini-SFINKS in wide temperature range. Temperature dependencies of unit cell parameters of the both compounds have a peculiarity at 200 *K* (fig.1,2). This fact perhaps points out a general character of such anomaly for the ceramics of 1—2—3 type. Similar effect has been found by ultrasonic studies. One can also see the dependence of Z-coordinate of Ba atom on temperature (fig3) which shows the anharmonism in the character of atoms oscillations.

The substitution of Cu by Fe in 1—2—3 system has also been studied using three different diffractometers: Mini-SFINKS, D2B, DMC. Averaging the obtained results we can say that Fe occupation in Cu la position is two times higher then Cu 2g position and there is no dependence on the type of ceramics (Sm—1—2—3, Y—1—2—3). Obviously, mixed valence state of Sm does not concern nonlinear dependencies of unit cell parameters on temperature. One more examination of structure effects due to the mixed valence state has been carried out by studying the couple $^{"0"}Sm_2CuO_{4+d}$ and $^{144}Nd_2CuO_4$ which can be compared with $Nd_{1.85}Ce_{0.15}CuO_{4+d}$ ($T_c = 25\ K$) and $Sm_{2-x}Ce_xCuO_{4+d}$ ($T_c = 15\ K$). Fig.4,5 show the results of neutron studies of $^{"0"}Sm_2CuO_{4+d}$ and $^{144}Nd_2CuO_4$ compounds and data from ref. [2], one can see that mixed valence state of Ce does not display itself in the temperature dependencies of unit cell parameters. The temperature dependence of a — parameter for $^{"0"}Sm_2CuO_{4+d}$ is found to be similar to the one obtained for SmB_6. The experimental data represented above point out the connection between the valence instabilities and superconductivity phenomenon and require careful examination.

References

1. Trounov V.A. et al. Preprint LNPI-1708. Leningrad, 1991. 18 p.
2. Sadowski W. et al. //Physica. 1990. V.C170. P.103.