

V. V. LUPAREV¹, G. M. KUZ'MICHEVA¹, E. P. KHLYBOV^{2,3}, I. E. KOSTYLEVA^{2,3},
T. PALEWSKI²

¹Department of Solid State Physics and Chemistry, M. V. Lomonosov State Academy of Fine Chemical Technology, Moscow, Russia

²International Laboratory of High Magnetic Fields and Low Temperatures, Wroclaw, Poland

³L. F. Vereshchagin Institute for High Pressure Physics, Troitsk, Russia

The Particularities of Infinite-Layer Compounds $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ (Ln = La, Pr, Nd, Eu)

The superconducting phases with general formula $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ with Ln = La ($T_c = 24\text{...}40\text{K}$); Pr ($T_c = 30\text{...}44\text{K}$); Nd ($T_c = 8\text{K...}40\text{K}$); Eu ($T_c = 40\text{K}$) and non-superconducting phases of CaCuO_2 -type structure were prepared by high-pressure synthesis. The products were examined by X-ray powder diffraction. For the determination of composition Rietveld method was used. Structure investigations have shown that non-superconducting phases have oxygen vacancies. Within the Cu formal charge range from 1.81 to 1.93 the infinite layer cuprates exhibit superconductivity. Coexistence of both superconducting and non-superconducting phases of the CaCuO_2 -type structure in samples with Ln = Nd and Eu was found.

Keywords: infinite layer cuprates; oxygen vacancies; phase splitting; superconductivity

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1. Introduction

For the first time a simple infinite layer compound has been synthesized by Siegrist et al. It has been found later that compositions of $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ (KUZ'MICHEVA et al., ER et al., ICEDA et al., PODLESNYAK et al., KORCZAK et al., LUPAREV et al., SMITH et al. and ZHOU et al.) with Ln= La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho and Y were stabilized in the infinite layer structure using synthesis under high pressure. The $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ ($\delta \geq 0$) crystallizes in the CaCuO_2 -type structure where sites of calcium are occupied by strontium or rare-earth elements (see Fig.1) and demonstrate both superconducting and non-superconducting properties. The CaCuO_2 is the simplest structure containing CuO_2 layers, the structure unit essential to high- T_c superconductivity (SC), which alternate with oxygen-free layers of Ca along the z -axis. Besides CaCuO_2 unit is the least structural fragment of all perovskite-like high-temperature superconductors.

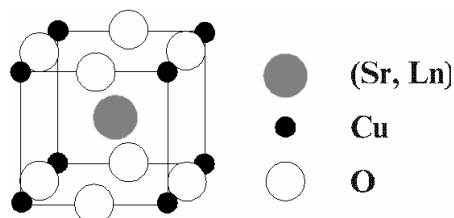


Fig. 1: The unit cell of $(\text{Sr,Ln})\text{CuO}_{2-\delta}$ phases with the CaCuO_2 -type structure

Here we report the results of the X-ray diffraction study and also magnetic and electrical measurements of the phases $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ ($x = 0.05\text{--}0.20$; $\delta = 0\text{--}0.10$; Ln = La, Pr, Nd, Eu). Obtained results support the opinion that absence of SC is associated with oxygen vacancies. The coexistence of superconducting and non-superconducting phases was found in the samples of $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ with Ln = Nd and Eu.

2. Experimental

Infinite layer polycrystalline samples with the general composition $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ ($y=0.05\text{--}0.20$; Ln = La, Pr, Nd, Eu) have been synthesized in two stages. Appropriate oxides of SrO (or SrCO_3), Ln_2O_3 and CuO in stoichiometric proportion were mixed in agate mortar, pressed into pellets and annealed at temperature $t=860\text{--}900^\circ\text{C}$ during $\tau=8\text{--}20$ hours in air with intermediate regrinding after preliminary calcination at 200° . During the second stage the samples were thoroughly powdered, pressed into pellets of $8\text{--}10$ mm in diameter and $2\text{--}3$ mm thick and put into molybdenum (or tungsten) foil and hexagonal boron nitride to isolate ones from the graphite heater. Then the samples were heated under high pressure. The parameters of high pressure synthesis were: $p=4\text{--}8$ GPa, $t=750\text{--}1000^\circ\text{C}$, $\tau=5\text{--}45$ min (samples *a*).

A number of the samples $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ ($\delta \geq 0$) have been synthesized by the method described by Podlesnyak et al. The starting mixture of SrCuO_2 and LnCuO_2 phases in the required ratio was heated under a pressure of $3.5\text{--}6$ GPa at $t=900\text{--}1200^\circ\text{C}$ for $\tau=30$ min (samples *b*).

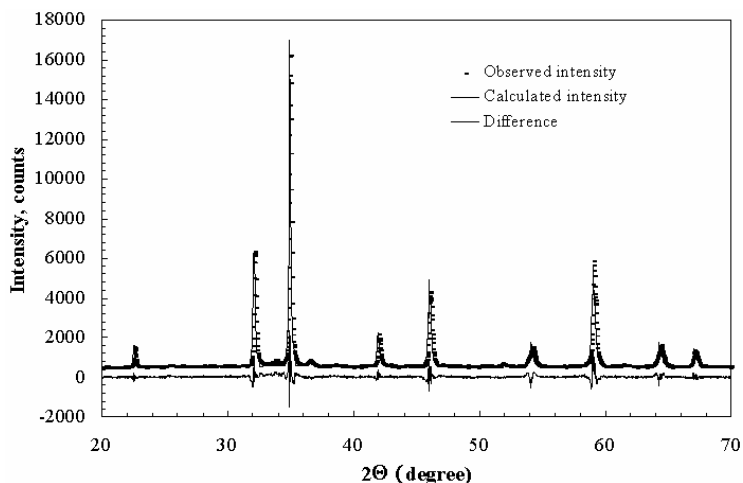


Fig. 2: XRD pattern of $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_{2-\delta}$ and final Rietveld difference plots

X-ray powder diffraction (XRD) examination has been performed using a DRON-3 and HZG-4 diffractometers (CuK_α radiation, graphite monochromator). The angular positions of diffraction peaks were refined by the full-profile least-squares method. The line shape was approximated by the convolution of Gauss and Lorentz functions. The qualitative phase analysis was performed using the PDF-2 database and original works. Phase contents have determined using the DBWS program (version 9411). A least-squares method was used to refine lattice parameters of the $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ phases.

The compositions of infinite layer phases were refined with the Rietveld method using DBWS program. Intensities were measured between 10° and 130° (2θ) with increments of

0.02° and exposition of 10+20 s. Peak shapes were treated assuming a pseudo-Voigt profile function and intensities were calculated over an angular range of eight full-widths at half maximum. The starting structural model chosen was identical for all phases: $\text{Sr}_{0.80}\text{La}_{0.20}\text{CuO}_2$ with isotropic thermal parameters B_{iso} for (Sr,Ln), Cu, and O atoms equal to 0.4, 0.6, and 1.0, respectively, and with the complete site occupancies. The first step involved the refinement of the scale factor, background parameters, cell parameters, the counter "zero", and profile parameters. Because of the strong correlation between the isotropic thermal parameters B_{iso} and the site occupancies p , the p values for all atoms (excluding Cu) were refined at the second step and were taken as constant in further refinement. The B_{iso} values for all atoms were calculated at the last step.

Electrical resistance and magnetic susceptibility were measured by the standard four-probe method and induction method, respectively, from 300 K down to 4.2K. The electric and magnetic measurements were used to determine values of critical temperature (T_c) of superconducting transition.

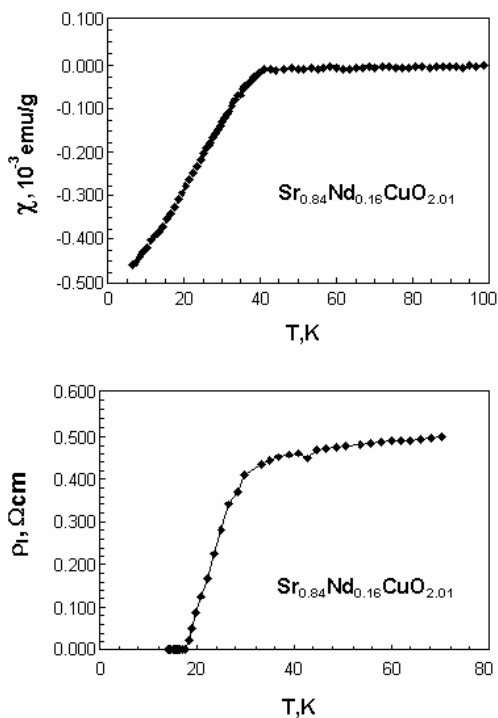


Fig. 3: Temperature dependencies of the magnetic susceptibility (upper part) and the electrical resistivity (lower part) for phase of refined composition $\text{Sr}_{0.84}\text{Nd}_{0.16}\text{CuO}_{2.01(5)}$

3. Results and discussion

Powder X-ray diffraction (XRD) indicates that tetragonal phases with CaCuO_2 -type structure (space group: $P4/mmm$, $z=1$) have been obtained for all systems. The patterns of the samples *a* reveal less than 10% of impurity phases such as Cu_2O , CuO , SrCuO_2 , Ln_2CuO_4 in addition to the major CaCuO_2 -type structure phase. The method of syntheses *b* allows to get nearly single phase samples (for example, see fig. 2). The superconducting phases have been obtained from nominal compositions of $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ for $\text{Ln} = \text{La}$ ($x=0.07$ and $T_c=24$

K); Ln = La ($x=0.12$ and $T_c = 40$ K); Ln = Pr ($x = 0.12$ and $T_c = 44$ K); Ln = Pr ($x = 0.16$ and $T_c = 30$ K); Ln = Nd ($x = 0.05$ and $T_c = 30$ K); Ln = Nd ($x = 0.10$ and $T_c = 18$ K); Ln = Nd ($x=0.12$ and $T_c = 8$ K); Ln = Nd ($x = 0.13$ and $T_c = 35$ K); Ln = Nd ($x = 0.15$ and $T_c = 40$ K) and Ln = Eu ($x = 0.07$ and $T_c = 40$ K). The Fig. 3 shows as an example the results of magnetic (upper part) and electric (lower part) measurements for samples with nominal formula $\text{Sr}_{0.85}\text{Nd}_{0.15}\text{CuO}_{2-\delta}$. It can be seen that rapid decrease of magnetic susceptibility and electrical resistance begins at temperature equal to 40 K.

Table 1: Refined structural parameters for $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ (Ln=La, Pr) phases. Constrains are $p(\text{Sr})+p(\text{Ln})=1$.

Data	Nominal composition			
	$\text{Sr}_{0.93}\text{La}_{0.07}\text{CuO}_{2-\delta}$	$\text{Sr}_{0.93}\text{La}_{0.07}\text{CuO}_{2-\delta}$	$\text{Sr}_{0.84}\text{Pr}_{0.16}\text{CuO}_{2-\delta}$	$\text{Sr}_{0.93}\text{La}_{0.07}\text{CuO}_{2-\delta}$
Condition of synthesis	P=5GPa, $t=950^\circ\text{N}$, $\tau=5$ min	P=5GPa, $t=950^\circ\text{N}$, $\tau=30$ min	P=5GPa, $t=950^\circ\text{N}$, $\tau=30$ min	P=5GPa, $t=950^\circ\text{N}$, $\tau=5$ min
Critical temperature: T_c , [K]	No SC. up to 4.2 K	24	30	No SC. up to 4.2 K
Lattice parameters:				
a , [\AA]	3.9310(7)	3.9386(6)	3.9492(4)	3.9284(3)
c , [\AA]	3.423(1)	3.414(1)	3.3833(6)	3.4331(5)
Site occupancies:				
$p_{\text{Sr}}/p_{\text{Ln}}$	0.92(1)/0.08	0.86(1)/0.14	0.83(1)/0.17	0.94(3)/0.06
Isotropic thermal parameter: B_{iso} , [\AA^2] of (Sr,Ln)	0.65(4)	1.51(4)	1.58(7)	1.28(4)
Site occupancies:				
p_{Cu}	1.00*	1.00*	1.00*	1.00*
Isotropic thermal parameter: B_{iso} [\AA^2] of Cu	0.56(6)	0.66(6)	1.4(1)	1.27(5)
Site occupancies:				
p_{O}	1.89(2)	1.98(2)	2.02(4)	1.89(6)
Isotropic thermal parameter: B_{iso} [\AA^2] of O	0.5(1)	0.8(1)	0.8(2)	1.2(1)
R_{WP} , %	4.91	5.68	6.32	5.87
R_p , %	3.82	4.41	4.61	4.21
R_F , %	3.91	6.87	6.29	4.92
R_B , %	4.33	8.46	6.80	4.50
$S=R_{\text{WP}}/R_{\text{EXP}}$	1.56	1.78	2.66	2.55

Note: * - fixed parameter; R_{WP} - the weighted pattern R-factor, R_p - the pattern R-factor, R_B - the R-value for Bragg intensities, R_F - the R-value based on the deduced "observed" and calculated amplitudes; R_{EXP} - the expected pattern R-factor

In the Tables 1...3 are listed the final refinement of the isotropic thermal parameters (B_{iso}) and occupancies (p) in some studied $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ phases. As a rule, the occupancy of oxygen atoms is smaller than unity for non-superconducting phases (see Table 1 and Table 3). The superconducting phases have full occupancy of the oxygen sites (p_{O} equal to 2 within experimental error).

Table 2: Refined structural parameters for $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_{2-\delta}$ phases. Constrains are $p(\text{Sr})+p(\text{Nd})=1$.

Data	Nominal composition	
	$\text{Sr}_{0.87}\text{Nd}_{0.13}\text{CuO}_{2-\delta}$	$\text{Sr}_{0.85}\text{Nd}_{0.15}\text{CuO}_{2-\delta}$
Critical temperature: T_c , [K]	35	40
Lattice parameters: a , [\AA]	3.9453(5)	3.944(1)
c , [\AA]	3.3836(9)	3.399(1)
Site occupancies: $p\text{Sr}/p\text{Nd}$	0.83(1)/0.17**	0.86(1)/0.14
Isotropic thermal parameter: B_{iso} [\AA^2] of (Sr,Nd)	0.92(3)	1.3(1)
Site occupancies: $p\text{Cu}$	1.00*	1.00*
Isotropic thermal parameter: B_{iso} [\AA^2] of Cu	0.97(4)	0.7(2)
Site occupancies: $p\text{O}$	2.00(2)	2.00(2)
Isotropic thermal parameter: B_{iso} [\AA^2] of O	0.89(9)	3.2(6)
R_{WP} , %	8.68	8.51
R_p , %	6.30	7.94
R_F , %	8.37	9.57
R_B , %	9.53	9.95
$S=R_{\text{WP}}/R_{\text{EXP}}$	2.28	2.32

Note: * - fixed parameter, ** - the calculation for averaged composition

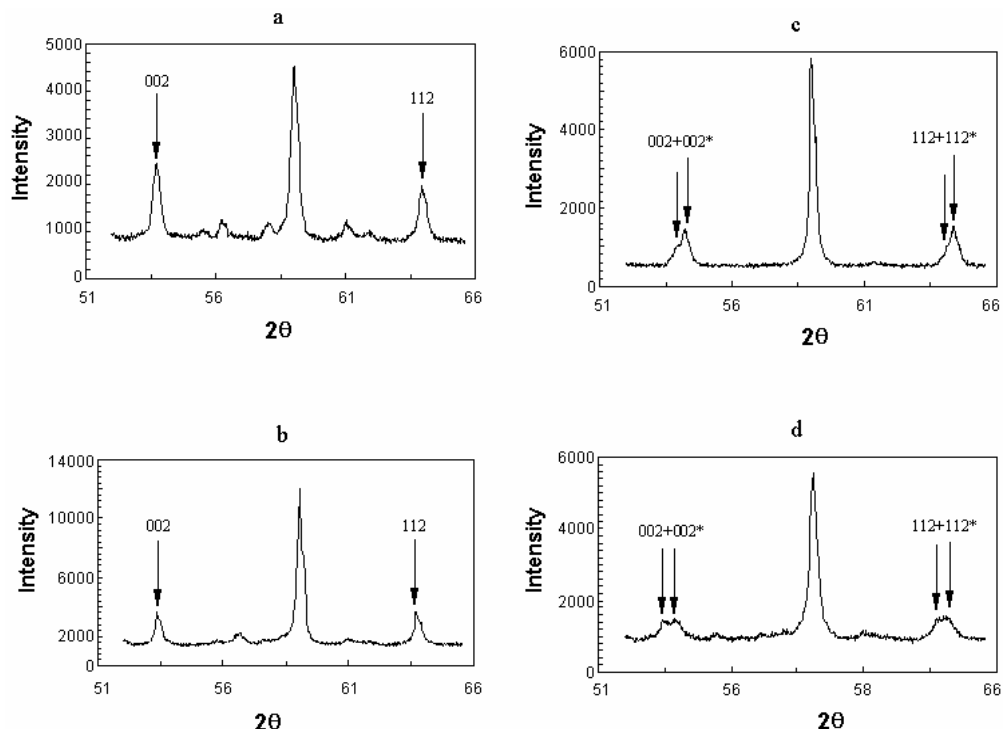


Fig. 4: Part of powder diffraction patterns of $\text{Sr}_{0.92(1)}\text{La}_{0.08}\text{CuO}_{1.89(2)}$ (a), $\text{Sr}_{0.83(1)}\text{Pr}_{0.17}\text{CuO}_{2.02(4)}$ (b), $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_2$ (averaged composition $\text{Sr}_{0.83(1)}\text{Nd}_{0.17}\text{CuO}_{2.00(2)}$), coexistence of two phases with $a=3.944(1)$, $c=3.399(1)$ and $a^*=3.9453(5)$, $c^*=3.3836(9)$, data in [\AA] (c), $\text{Sr}_{1-x}\text{Eu}_x\text{CuO}_{2-\delta}$ (coexistence of two phases: $\text{Sr}_{0.98(1)}\text{Eu}_{0.02}\text{CuO}_{1.96(3)}$ with $a=3.930(1)$, $c=3.426(2)$ and $\text{Sr}_{0.92(1)}\text{Eu}_{0.08}\text{CuO}_{2.03(3)}$ with $a^*=3.932(1)$, $c^*=3.402(2)$, data in [\AA] (d).

We obtained correlation between the transition temperature and the formal charge of Cu atoms (FC Cu) for $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_{2-\delta}$ samples calculated from the electroneutrality condition of refined phase compositions (Table 1÷4). We have been found that in the range of the FC Cu of 1.81-1.93 the infinite layer cuprates show superconductivity properties.

The occurrence of oxygen interstitial in the position 0 0 1/2 (as suggested by Podlesnyak et al. on the basis of neutron diffraction data) was neither proven nor confirmed. In contrast to neutron diffraction X-ray examination allowed to determine the Sr:Nd ratio. The T_c varies with cation composition and reaches the maximum value of 40K around $y=0.14\dots 0.16$ for $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_{2-\delta}$ and $y=0.08$ for $\text{Sr}_{1-x}\text{Eu}_x\text{CuO}_{2-\delta}$ systems.

Table 3: Refined structural parameters for $\text{Sr}_{1-x}\text{Eu}_x\text{CuO}_{2-\delta}$ phases. Constrains are $p(\text{Sr})+p(\text{Eu})=1$.

Data	Nominal composition		
	$\text{Sr}_{0.93}\text{Eu}_{0.07}\text{CuO}_{2-\delta}$	$\text{Sr}_{0.85}\text{Eu}_{0.15}\text{CuO}_{2-\delta}$	
Critical temperature:			
T_c , [K]	40	No SC. up to 4.2 K	No SC. up to 4.2 K
Lattice parameters:			
a , [Å]	3.932(1)	3.930(1)	3.9421(7)
b , [Å]	3.402(2)	3.426(2)	3.371(1)
Site occupancies:			
$p\text{Sr}/p\text{Eu}$	0.92(1)/0.08	0.98(2)/0.02	0.79(1)/0.21
Isotropic thermal parameter:			
B_{iso} [Å ²], of (Sr/Eu)	0.67(11)	1.15(11)	0.94(6)
Site occupancies:			
PCu	1.00*	1.00*	1.00*
Isotropic thermal parameter			
B_{iso} [Å ²] of Cu	0.3(2)	0.2(1)	0.86(8)
Site occupancies:			
PO	2.03(3)	1.96(3)	1.94(3)
Isotropic thermal parameter B_{iso} [Å ²] of O	0.03(24)	0.9(2)	0.9(2)
R_{WP} , %		4.65	4.38
R_p , %		3.63	3.37
R_F , %	4.41	3.88	4.87
R_B , %	3.99	3.58	4.93
$S=R_{WP}/R_{EXP}$		1.55	1.93

Note: * - fixed parameter

Table 4: The X-ray study of $\text{Sr}_{1-x}\text{Nd}_x\text{CuO}_{2-\delta}$

Sample	Nominal composition	Refined composition
(I)	$\text{Sr}_{0.84}\text{Nd}_{0.16}\text{CuO}_2$ ($T_c < 4.2$ K)	$\text{Sr}_{0.91}\text{Nd}_{0.09}\text{CuO}_{1.98(3)}$
(II)	$\text{Sr}_{0.85}\text{Nd}_{0.15}\text{CuO}_2$ ($T_c = 40$ K)	$\text{Sr}_{0.86}\text{Nd}_{0.14}\text{CuO}_{2.00(2)}$
(III)	$\text{Sr}_{0.85}\text{Nd}_{0.15}\text{CuO}_2$ ($T_c = 40$ K)	$\text{Sr}_{0.84}\text{Nd}_{0.16}\text{CuO}_{2.01(3)}$
(IV)	$\text{Sr}_{0.87}\text{Nd}_{0.13}\text{CuO}_2$ ($T_c = 35$ K)	$\text{Sr}_{0.83}\text{Nd}_{0.17}\text{CuO}_{2.00(2)}$
(V)	$\text{Sr}_{0.90}\text{Nd}_{0.10}\text{CuO}_2$ ($T_c = 18$ K)	$\text{Sr}_{0.81}\text{Nd}_{0.19}\text{CuO}_{2.00(4)}$
(VI)	$\text{Sr}_{0.925}\text{Nd}_{0.075}\text{CuO}_2$ ($T_c < 4.2$ K)	$\text{Sr}_{0.87}\text{Nd}_{0.13}\text{CuO}_{1.95(2)}$

Note: I, III, V - samples a; II, IV, VI - samples b

In $\text{Sr}_{1-x}\text{Ln}_x\text{CuO}_{2-\delta}$ systems a coexistence of two isostructural phases with near composition takes place (see Fig. 4, part c and d). There is a clear tendency of increasing reflections splitting by a reduction of Ln ionic radius. The most splitting of reflections is found for $\text{Sr}_{1-x}\text{Eu}_x\text{CuO}_{2-\delta}$ system (Fig. 4, part d). The results of X-ray diffraction and electrophysical properties provide evidence for the formation of non-superconducting and superconducting phases. It is obvious that the anomalous phase disintegration is due to the fluctuating valence state of Cu. According to Kuz'micheva, a necessary condition for high-temperature superconductivity is the presence of the cation that not only exhibits a variable formal charge, but that also characterizes by the fluctuating valence state. In particular, phases including such a cation possess a large compressibility and phase splitting. A preliminary study of the $\text{Sr}_{1-x}\text{Eu}_x\text{CuO}_{2-\delta}$ system by KUZ'MICHEVA et al. seems to confirm this assumption. All these observations are helpful for understanding the mechanisms of high temperature superconductivity and they are useful for searching new superconductors.

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Contact information:

PhD LUPAREV V.V., Professor Dr. sc. hab. KUZ'MICHEVA* G.M
Department of Solid State Physics and Chemistry
M. V. Lomonosov State Academy of Fine Chemical Technology
86 Vernadsky prosp.
117571, Moscow
Russia

Dr. sc. hab. KHLYBOV E.P., PhD KOSTYLEVA I.E.
L. F. Vereschagin Institute for High Pressure Physics
142090, Troitsk
Russia

e-mail: khlybov@ns.hppi.troitsk.ru

Doc. Dr.sc. hab PALEWSKI T.
International Laboratory of High Magnetic Fields and Low Temperatures
Wroclaw
Poland

e-mail: paltom@alpha.mlspmint.pan.wroc.pl

*corresponding author
e-mail: galkuz@orc.ru