Experimental report

03/02/2017

Proposal: 5-14-260 **Council:** 4/2016

Title: Nuclear structures of one-dimensional spins chains cuprates SrCu0.99M0.01O2 with M=(Mg, Zn or Pd) and Sr0.99R0.01CuO2 with R=(K or La)

Research area: Materials

This proposal is a new proposal

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Samples: Sr0.99K0.01CuO2
SrCu0.99Pd0.01O2
Sr0.99La0.01CuO2
SrCu0.99Mg0.01O2
SrCu0.99Zn0.01O2

Instrument	Requested days	Allocated days	From	To
D9	30	10	25/08/2016	04/09/2016

Abstract:

Thermal management is of major interest in the field of power electronics, especially in novel devices such as increasingly miniaturized microchips, batteries or solar panels. Single crystalline spin chain cuprates such as the pristine SrCuO2 exhibit an anisotropic thermal conductivity arising both from phonons scattering mechanisms and magnetic excitations occurring along the spin chains crystallographic direction (c-axis). A substituted, on strontium or on copper site SrCuO2 single crystals were grown successfully, giving the formulas Sr0.99R0.01CuO2 with R=(La or K) and SrCu0.99M0.01O2 with M=(Mg, Zn or Pd). Determining atomic positions in this system and comparing them to those of the pristine one, is of crucial importance as this would help us to understand the magnetic excitations scattering processes: neutron diffraction experiments could determine precisely the atomic positions of the elements in the cell and more precisely the atomic positions of the oxygen/copper atoms in the spins chains

$SrCuO_2$ is a 1D Mott insulating spin ½ chains cuprate. This compound exhibits highly anisotropic and ballistic thermal transport properties along the spins chains direction, arising from two kinds of heat carriers: phonons and magnetic excitations (spinons). This compound crystallizes in an orthorhombic structure of the space group *Cmcm*. The crystal structure is given in **Fig.1.**

Along the c-axis, two parallel spins chains formed by alternating Cu-O-Cu ions, are found, distanced by one Cu-O bond length and where the copper is square planar coordinated. The superexchange interaction between two neighbouring copper ions within the chains is antiferromagnetic. This interaction happens through the oxygen bridge given a Cu-O-Cu bonding angle of ≈ 177.7° (from X-ray) and ≈ 178.1° (from powder neutron diffraction data). The heat conduction peak (convolution of transport by lattice and spin excitations) being centred at 28K [1,2], our study consists on probing the substitution effect (on the copper or strontium site) on both channels of propagation and more precisely, through spinons-defects and phonons-defects scattering mechanisms, in order to, further, control the temperature of occurrence of the thermal conduction peak. However, magnetic heat conduction is found to be highly sensitive to the geometry of the chains. Thus, the amount of introduced dopants is very low (max 1%) to unambiguously ascribe the following physical properties to the dopant.

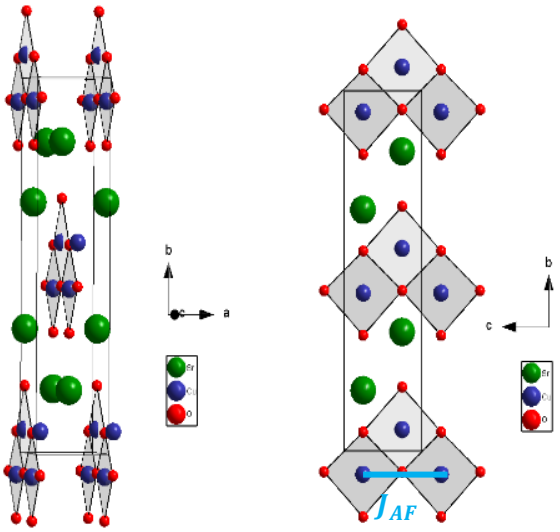

Fig. 1. Crystal structure or $SrCuO_2$ *(left)* Spin ½ chains in the [b,c] plane and the antiferromagnetic superexchange interactions within the chain J_{AF}

During this experiment, we proposed to investigate the nuclear structure of two single crystals of compositions $SrCu_{0.99}Mg_{0.01}O_2$ and $Sr_{0.99}La_{0.01}CuO_2$. While square planar Mg^{2+} possesses the same ionic radius as Cu^{2+} within the chains, the bonding angles of the chains should be conserved in this compound, while in the La-doped $SrCuO_2$, the dopant can locally induce local chains distortions because of the mismatch in the ionic radii of La and Sr, in addition, of the change of 1% Cu^{2+} within the chains to Cu^{+} moving their spins from S=1/2 to S=0.

To check the doping effect on the atomic positions and bonding angles in the crystal lattice, we chose to conduct the investigations at temperatures in such a way as to cross the heat conduction peak i.e. collect sets of reflections at T=20, 37, 50 and 300 K. To this aim, the samples have been fixed with cement onto an alumina pin, the whole has been mounted on the first circle. The crystals have been grown using the travelling solvent floating zone method.

In the case of the $Sr_{0.99}La_{0.01}CuO_2$, the number of collected reflections was of: 819, 670, 786 and 1198 for 20, 37, 50 and 300K respectively. As the expected structural changes are slight, due to the very low amount of doping, a sufficient number of high q reflections have been collected in order to highlight subtle modifications that are induced by the dopant, if any. The Rietveld structural refinement has been carried out using *Fullprof* Software, and the results yielded good values of χ^2 =2.64, 4.70, 2.07 and 1.18, respectively. Results of the structural refinement are given in **Tab.1.**

Table. I. Structural parameters of the 1% La-doped $SrCuO_2$ obtained through Rietveld structural refinement on the integrated intensity data .

	T=20K	T=37K	T=50 K	T= 300K	$SrCuO_2$ at T=300K
a	3,5641	3,5632	3,5635	3,5756	3,57
b	16,3173	16,3144	16,3125	16,3268	16,32
c	3,9122	3,9123	3,9119	3,9161	3,91
Sr (x=0, z=0.25)	0,33081(9)	0,3307(1)	0,3306(1)	0,33064(9)	0,3313
Cu (x=0, z=0.25)	0,0609(1)	0,0611(1)	0,0611(1)	0,0610(1)	0,0613
O1 (x=0, z=0.25)	0,9441(1)	0,9442(2)	0,9441(1)	0,9446(1)	0,9363
O2 (x=0, z=0.25)	0,1787(1)	0,1788(1)	0,1791(1)	0,1788(1)	0,1757
Cu-O1-Cu (≈180°)	175,1(3)	174,9(3)	174,9(3)	174,6(3)	177,7
Cu-O1-Cu (≈90°)	92,44(14)	92,53(15)	92,53(14)	92,69(13)	88,8522

The main result of the study resides in the elongation of the apical Cu-O2 (as shown on Fig. 2.) bond length upon La-doping compared to the pristine compound, giving rise to a change of the bonding angle Cu-O1-Cu within the chains from 177.7 to ~174.5°. This elongation has also been corroborated by EPR measurements along the three crystallographic axis. Indeed, only along the b-axis, the hyperfine coupling of the electronic spin to the nuclear spin has been evidenced due to the stronger coupling resulting from the increasing distance Cu-O2.

These results help us in understanding the impact of such a substitution on the magnetic heat conduction of this compound. Indeed, our last results show that: on the one hand, the mean free path of spinons in strongly reduced, undoubtedly due to the change of the geometry of chains that has been evidenced thanks to the experiment on D9, along with the creation of Cu^+ (S=0 quantum impurities within the chains) which goes along with the pseudo gap evidenced through inelastic neutron scattering experiments and results in an important decrease of the magnetic heat conduction (dropping from 800 to 20 W/m.K).

No structural or magnetic transition has been evidenced upon heating in this material, however, an increase of the integrated intensity of some reflections of the form (0k0) has been evidenced when going from 50 to 300K. The same feature has been observed during Low temperature X-ray diffraction experiments on a grinded single crystal at the same temperatures as during our experiment on D9. The reason to this might be due to a local change of symmetry of Cu^{2+} environment. This possibility is being investigated by the above mentioned EPR experiments.

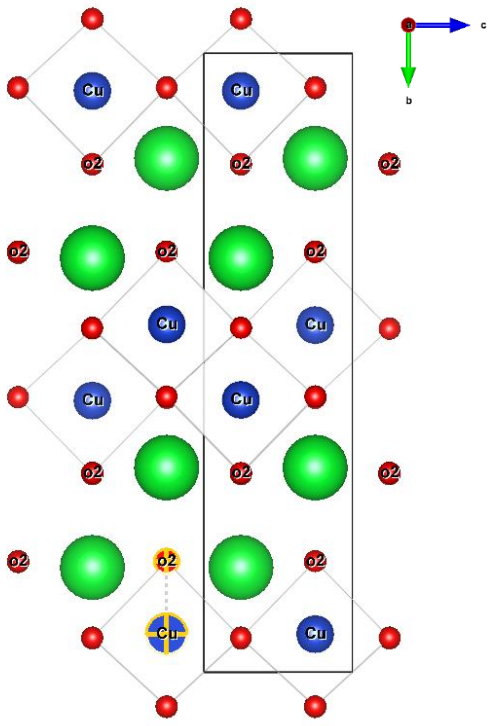

Fig. 2. Projection of the structure in the [b,c] plane showing the positions of the O2 atoms

On the second crystal of composition $SrCu_{0.99}Mg_{0.01}O_2$, only one set of reflections has been collected at 20K. Unfortunately, it turned out that the crystal was twinned and the structural refinement didn't give good agreement with the experimental data.

REFERENCES

[1] N. Hlubek, P. Ribeiro, R. Saint-Martin, A. Revcolevschi, G. Roth, G. Behr, B. Büchner, and C. Hess, Phys. Rev. B **81**, 020405 (2010).
[2] N. Hlubek, X. Zotos, S. Singh, R. Saint-Martin, A. Revcolevschi, B. Büchner, and C. Hess, J. Stat. Mech. Theory Exp. **2012**, P03006 (2012).