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*Sr<sub>1-x</sub>Ca<sub>x</sub>Cu<sub>2</sub>O<sub>4</sub>*

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Marie-Bernadette Lepetit, Alain Gellé. Charge order in the incommensurate compounds *Sr<sub>1-x</sub>Ca<sub>x</sub>Cu<sub>2</sub>O<sub>4</sub>*. Physica B: Condensed Matter, 2005, 359-361, pp.1258. hal-00004149

**HAL Id: hal-00004149**

**<https://hal.science/hal-00004149v1>**

Submitted on 3 Feb 2005

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# Charge order in the incommensurate compounds $Sr_{14-x}Ca_xCu_{24}O_{41}$

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## Abstract

The present paper studies, using ab-initio calculations, the influence of the incommensurate structural modulations on the low energy physics of the  $Sr_{14-x}Ca_xCu_{24}O_{41}$  oxides. On-site, nearest-neighbor and next-nearest-neighbor effective parameters were computed within a  $t - J + V$  model based on the copper oxide layers. The structural modulations appear to be the key degree of freedom, responsible for the low energy properties such as the electron localization, the formation of dimers in the  $x = 0$  compound or the anti-ferromagnetic order in the  $x = 13.6$  compound.

*Key words:* Charge order, incommensurate systems, spin chains, ab-initio electronic structure calculations.

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The  $Sr_{14-x}Ca_xCu_{24}O_{41}$  compounds are composed of alternate layers of weakly-coupled spin ladders and spin chains [1]. The two sub-systems have incommensurate translation vectors in the longitudinal chains and ladders direction with a pseudo-periodicity is of 10 chain units for 7 ladder units. The misfit of the two-subsystems induces a structural modulation of each of them with the periodicity of the other. The low energy properties of the  $Sr_{14-x}Ca_xCu_{24}O_{41}$  compounds are different both from those of uniform ladders and of uniform chains. In addition their electronic structure is strongly dependent on the substitution of the strontium by the isovalent calcium counter-ion.

Formal-charge analysis shows that these systems are intrinsically doped with six holes per formula unit (f.u.). Similar to high- $T_c$  superconductors, the spins are supported by  $3d$  orbitals of the  $Cu^{2+}$  ions while the holes are expected to be mainly supported by the oxygen  $2p$  orbitals and to form Zhang-Rice singlets [2] (ZRS). The hole repartition between the chain and ladder subsystems is still under debate. For the undoped compound, Madelung potential calculations [3] suggest a localization of the 6 holes on the chains.

X-ray [4] and optical conductivity [5] measurements however suggest that about one hole per f.u. may be located on the ladders. Under increasing  $Ca$  substitution, an increasing transfer of part of the holes to the ladders is observed [4,5,6]. X-rays suggest that only 1.1 hole is transferred for the  $x = 12$  compound, while optical conductivity and NMR show a larger hole transfer (resp. 2.8 for  $x = 11$  and 3.5 for  $x = 11.5$ ).

The chain subsystem is particularly intriguing since not only it exhibits a spin gap ( $\Delta_\sigma \simeq 11 - 12$  meV [7,8] for  $x = 0$ ), but it also presents a low temperature magnetic behavior strongly dependent of the  $Ca$  content. Indeed, the undoped compound exhibit a charge order at  $T < 240K$  [9] as well as spin dimerization [7]. These dimers are seen to be ordered [11,10] according to a 5 sites pseudo-periodicity where second-neighbor dimers are separated by two ZRS. The charge order disappear with  $Ca$  doping ( $x > 8$ ) even-though the magnetic interactions within and between the dimers seem to remain unchanged. At large doping ( $x \geq 11$ ) and very low temperatures ( $< 2.5K$ ) an antiferromagnetically ordered phase is observed [12].

These properties cannot be accounted for in a homogeneous hole-doped spin-chain model. One can thus look for their origin toward the effects of the incommensurate structural modulations. We thus evaluated

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the parameters of a second neighbor  $t - J + V$  model, as a function of the modulation parameter, using embedded-fragment spectroscopy ab initio calculations [13]. The calculations have been performed for two different doping, namely for the  $Sr_{14}Cu_{24}O_{41}$  and  $Sr_{0.4}Ca_{13.6}Cu_{24}O_{41}$  compounds in their low temperature phase [1].

As expected the NN effective exchange are essentially ferromagnetic in nature while the second neighbor exchanges are antiferromagnetic and weakly modulated. In the  $x = 0$  compound, the NN exchange modulations are weak (standard deviation  $\sim 12\%$  of the average value:  $21.3 meV$ ). On the contrary, in the  $x = 13.6$  system the modulations are very large (standard deviation  $\sim 110\%$  of the average value:  $10 meV$ ). For a small part of the modulation distribution the distortions are such that the NN exchange becomes antiferromagnetic. Similarly the hopping integrals are very strongly modulated.

The main surprise however is the modulations of the on-site orbital energies (see figure 1). Indeed, they vary in a range of a few electron-Volts, that is much larger than any other parameter in the model (the next largest effective integrals are the NN hopping integrals that range between  $60 meV$  and  $200 meV$  for  $x = 0$  and from  $-70 meV$  to  $250 meV$  for  $x = 13.6$ ). This strong on-site energy variation is thus dominating the compounds physics through the spin localization on the low energy sites.

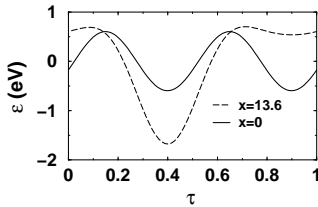


Fig. 1. Orbital energies as a function of the structural chain modulation parameter  $\tau$ .

Let now use these energies to locate the spins along the chains for several hypotheses of hole filling, namely  $n = 0, 1$  per f.u. for  $x = 0$  and  $n = 1, 2, 3$  for  $x = 13.6$  (see figure 2). For  $x = 0$  and all the holes on the chains, the computed spin arrangement retrieves the experimentally observed second-neighbor dimeric units as well as the correct number of free spins (computed : 0.5 per f.u., magnetic susceptibility measurements : 0.55). For  $x = 13.6$ , one observes the formation of low-spin clusters, with NN spins and no second-neighbor dimeric units. It is noticeable that the existence of antiferromagnetic NN exchanges allow these clusters to be low spin and to present low frustration of both NN and NNN exchanges (at most one frustrated NNN interaction). These results should be put into perspective with the antiferromagnetic ordering seen in magnetic

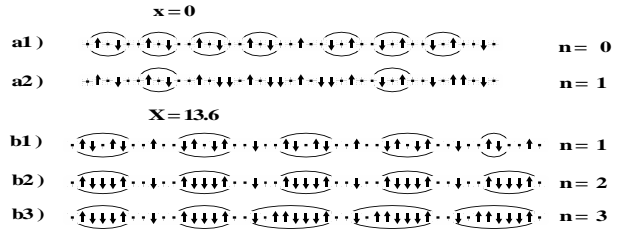


Fig. 2. Localization of the magnetic electrons along the chain, as a function of the number  $n$  of holes transferred to the ladders. a) for  $x = 0$ , b) for  $x = 13.6$ . Squares stand for ZRS, the ellipsoids delimit magnetically stable spin clusters.

susceptibility and ESR measurements. For  $n = 1, 2$  one still observes a large number of free spins, while for  $n = 3$  they essentially disappeared, in better agreement with magnetic susceptibility experiments [12].

We have studied the importance of the structural modulations on the low energy physics of the  $Sr_{14-x}Ca_xCu_{24}O_{41}$  family. Surprisingly these distortions are not simply responsible for weak parameters modulations around their average value, but induce very large variations of the orbital energies, effective hoppings and exchanges. This is the variation of the orbital energies that is responsible for the low energy properties of the compounds, through the localization of the magnetic electrons. It is in particular responsible for the formation of second neighbor dimers in the undoped compound and of stable low-spin clusters in the highly doped one.

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