Influence of the incommensurability in \( \text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}O_{41} \) family compounds.

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(Dated: January 14, 2022)

The present paper studies the influence of the structural modulation on the low energy physics of the \( \text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}O_{41} \) oxides, using ab-initio determination of the on-site and nearest neighbor effective parameters. The structural modulations appears 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.

PACS numbers: 71.10.Fd, 71.27.+a, 71.23.Ft

The family of \( \text{Sr}_{14-x}\text{Ca}_x\text{Cu}_{24}O_{41} \) transition-metal oxides has attracted a lot of attention in the last decade. Indeed, the superconducting state observed in the \( x > 11.5 \) compounds under high pressure [1], is supposed to be the realization of the remarkable theoretical prediction of superconductivity in two-legs doped spin ladders [2]. Moreover, this family of compounds exhibits a large diversity in electric and/or magnetic properties when chemical — isovalent substitution of \( \text{Sr} \) by \( \text{Ca} \) — and physical pressure are applied. For instance, under applied pressure, the compounds change from semi-conductor to conductor and finally to superconductor.

This family of compounds possesses a complex layered structure of two alternating subsystems [3]. The layers of the first subsystem are composed of weakly-coupled \( \text{CuO}_2 \), spin-1/2 chains along the c direction. The spins, supported by 3\( d \) orbitals of the \( \text{Cu}^{2+} \) ions, are coupled via two 90°\( \text{Cu}–\text{O}–\text{Cu} \) bonds. The layers of the second subsystem are composed of weakly-coupled, two-leg spin-1/2 ladders also along the c direction. The spins are strongly antiferromagnetically coupled on both legs and rungs, due to the 180°\( \text{Cu}–\text{O}–\text{Cu} \) bonds. The cell parameters of the two subsystems, in the direction of both chains and ladders, are incommensurate. The compounds have a pseudo-periodicity of 10 chain units for 7 ladder units.

Electro-neutrality analysis shows that these systems are intrinsically doped with six holes by formula unit (f.u.). Similar to high-\( T_c \) superconductors, the holes are expected to be mainly supported by the oxygen 2\( p \) orbitals and to form Zhang-Rice \( \text{Cu}^{2+} \) singlets with the associated-copper hole. NEXAFS experiments [4] have later supported this assumption. A calculation of the Madelung potential [5] on the concerned oxygen sites suggests that for the undoped compound, \( \text{Sr}_{14}\text{Cu}_{24}O_{41} \), the chains exhibit a larger electro-negativity than the ladders, resulting in a localization of all the holes on the former. Different experiments [6, 7], however suggest that about one hole per f.u. is located on the ladders.

Under \( \text{Ca} \) substitution, the same experiments, as well as \( \text{Cu} \) NMR [8], show a transfer of part of the holes to the ladders. However the precise number of transferred holes is still under debate. X-ray data [9] suggest a small hole transfer to the ladders (1.1 for \( x = 12 \)), while optical conductivity [10] and \( \text{Cu}^{63} \) NMR studies [8] show a larger hole transfer, of respectively 2.8 (\( x = 11 \)) and 3.5 (\( x = 11.5 \)).

Let us first focus on the undoped system, \( \text{Sr}_{14}\text{Cu}_{24}O_{41} \). This is a semiconductor with a 0.18 eV gap. The spin ladders have a singlet ground state with a spin gap of about 35 — 47 meV [8, 9, 10]. Surprisingly the spin chains also exhibit a singlet ground state with a spin gap of 11 — 12 meV [10, 11, 12, 13, 14]. Since homogeneous spin chains are known to be gap-less in the spin channel, the existence of a gap witnesses their strongly inhomogeneous character. In fact, the electronic structure of the \( \text{Sr}_{14}\text{Cu}_{24}O_{41} \) chains is usually understood as formed by weakly interacting dimmers [2, 14, 15, 16]. It is now well established that these dimers are formed by second-neighbor spins separated by a Zhang-Rice singlet (ZRS), and order [11, 12, 17, 18] according to a pseudo periodicity of 5 sites (one dimer followed by two ZRS).

When \( \text{Sr} \) is substituted by \( \text{Ca} \) the system becomes more metallic. The doped compound with \( x = 10 \) shows a gap of only 0.023eV [14]. This increased conductivity, as a function of the \( \text{Ca} \) doping, is usually understood as a consequence of the hole transfer from the chains to the ladders, in which the conduction is supposed to occur. However, a possible enhancement of the holes mobility within the chains is also evoked [2, 17]. Neutron scattering experiments [18] showed that the dimerization becomes unstable with \( \text{Ca} \) substitution and disappears for \( x > 8 \), although the magnetic interactions within and between the dimers remain unchanged. In parallel, both ESR [17] and thermal expansion data [13] witness a progressive disappearance of the charge order with increasing doping. Finally, at large doping (\( x \geq 11 \)) and very low temperatures (< 2.5K) an anti-ferromagnetic phase is observed [17, 19].

An important aspect of these compounds, which is most of the time neglected, is the modulation of the two subsystems. Indeed, the mutual influence of the two subsystems results in a modulation of each of them with the periodicity of the other. These distortions are particularly large on the chains. Indeed, in the highly doped systems, the \( \text{Cu}–\text{O}–\text{Cu} \) angle varies between 89°
and 99°, while the Cu–O distance varies with an amplitude of 19%. The magnetic interactions being very sensitive to both bond angles and distances between the magnetic sites and the bridging ligands, one can expect that the modulations will be of importance for the low energy physics of the compounds. In the ladder sub-system, the structural distortions are of weaker amplitude since the alkaline-earth counter-ions are attached to it. In addition, the Cu–O–Cu angle varies around \( \theta = 180° \) and therefore super-exchange mechanism (that scales as \( \cos^4 \theta \approx 1 - 2\theta^2 \)) should be dominant. Thus, while the effect of the structural modulations on the ladders may be of importance, it can be expected to be much weaker than on the chains sub-system.

The aim of this paper is to study to which extent the modulations influence the chains electronic structure. For this purpose, we performed ab-initio calculations so that to accurately evaluate the influence of the modulations on the magnetic orbital energies (OE) and nearest neighbors (NN) interactions. We choose for these calculations the \( \text{Sr}_1\text{Cu}_{23}\text{O}_{41} \) and \( \text{Sr}_{0.4}\text{Cu}_{1.6}\text{Cu}_{23}\text{O}_{41} \) compounds in their low temperature phase 20.

As the interactions between magnetic sites are essentially local, they can be accurately determined using an embedded fragment ab-initio spectroscopy method 21. The fragment includes the magnetic centers, the bridging oxygens mediating the interactions, and their first coordination shell. Short-range crystal effects are thus treated explicitly while the long-range crystal effects, such as the Madelung potential, are treated within an appropriate bath. The calculations have been performed using the DDCI method 22, a selected multi-reference single and double configuration interaction that properly treats (i) the strongly correlated character of the system, (ii) the mediation of the interaction via the bridging ligands and (iii) the screening effects on these processes 23. The reference space has been chosen to be composed by the copper magnetic orbitals. The basis sets are of valence \( 3\zeta \) 24 quality for \( \text{Cu} \) and \( 2\zeta + p \) for \( \text{O} \). This method has proved to be very accurate in the determination of the the local effective interactions as well as local electronic structures. One can cite, for instance, the remarkable results obtained on the effective exchange and hopping determination in high-\( T_c \) parent compounds 25, copper chains 26, and ladder 27 systems, where the computed values are within experimental accuracy, as well as on the charge ordering in the sodium vanadate low temperature phase 28.

Singlet-triplet excitation energies on embedded \( \text{Cu}_2\text{O}_6 \) fragments will thus yield the effective exchange integrals, while the first doublet-doublet excitation energies and associated wave functions yield both magnetic (hole) OE and hopping effective integrals. In order to study the influence of the incommensurability on these parameters, we performed calculations on 11 fragments associated to successive cells of the chain sub-system.

Let us first look at the hole OE (fig. 1). One sees immediately that their modulations are very large. Indeed, in the non-doped system, the OE vary within a range of 1.2 eV. In the Cu doped system, the variation is even much larger and spans a 2.2 eV range. Let us notice, that in both systems, the OE variation is larger than the hopping and exchange energy scales (respectively of 150 meV and 20 meV, see below). Thus, this is the OE that will dominate the low energy physics through the localization of the magnetic electrons (holes) on the low (high) energy sites. One should notice that the variations of the OE are due to the crystal distortions. Indeed, when using the average crystal structure — where the subsystems distortions have been omitted — the OE exhibit only very small variations 21 (< 30 meV for the undoped compound).

Before studying the electrons (holes) localization along the chain, let us take a look at the variations of the NN hopping and exchange interactions.

The effective exchange integrals, obtained for the 11 fragments, are reported in fig. 2. As expected the NN effective exchange for the \( x = 0 \) compound is ferromagnetic and exhibits small modulations around an average value of 21.3 meV, the standard deviation being 2.5 meV. On the contrary, the \( x = 13.6 \) compound does not follow the expectations. Indeed, the effective exchange varies
greatly, going from ferromagnetic values (20 meV) up to anti-ferromagnetic interactions as large as −10 meV. These anti-ferromagnetic interactions are observed either for large Cu–O–Cu angles (≃ 98°) or for large angles between the two magnetic orbitals (> 10°) associated with short Cu–Cu distances. In both cases, these strong distortions allow super-exchange mechanism to take place.

The effective hopping integrals between NN copper atoms are expected to be quite small, since the nearly tortious allow super-exchange mechanism to take place. The values as large as 208 meV present very large modulations and can reach the observed in our calculations (see fig. 2) since the hopping integrals present very large modulations and can reach large for the Cu–O–Cu angles forbid the through-bridge contribution via the oxygen orbitals. However, this is not what is observed in our calculations (see fig. 2) since the hopping integrals present very large modulations and can reach values as large as 208 meV for x = 0 and 266 meV for x = 13.6. These amplitudes are as large as 1/3 of the hopping observed in systems with 180° Cu–O–Cu angles, such as high-Tc superconductors [25] or CuO3 corner-sharing chains [26].

At this point it is clear that, the systems modulations, and the variations of these modulations according to the Cu doping, are crucial for the low energy properties of this family of iso-electronic compounds. We will now study whether they can explain the existence of the dimerization that is observed in the weakly doped compounds but not in the highly doped ones. For this purpose we need to extrapolate the values of the OE over the whole chain. It is usual to do so using a Bond Valence Sum (BVS) analysis, that analyzes the distances between the metal atom and its first coordination shell. However, for the Sr_{0.4}Ca_{1.6}Cu_{24}O_{41} system, the BVS analysis yields quite different results from the OE. A further analysis discloses that, in these systems, the Madelung potential on the magnetic centers, and thus the OE, is sensitive to the atomic displacements not only of the first coordination shell, but up to the 8th shell of neighbors. This is for this reason that the BVS analysis fails to correctly reproduce the copper valence for this type of compounds.

In order to extrapolate the OE over the whole chain, we used the crystallographic description of the incommensurate structure in a four dimensional space. Each subsystem is thus described by the three a, b and c usual spatial dimensions and a fourth coordinate τ that has the periodicity of the other subsystem and describes the modulations [30]. We fitted the computed values using a Fourier analysis as a function of τ (see fig. 3). One can note that the doped and undoped compounds present very different OE curves as a function of τ. Let us notice on fig. 4a the half periodicity of the magnetic cell for the Sr_{14}Cu_{24}O_{41} compound, observed in neutrons scattering experiments [11, 12].

Figure 4 reports the electrons (holes) localization along the chain as derived from the extrapolated on-site orbital energies. In the x = 13.6 case, a Fourier analysis has also been done on the effective NN exchange in order to predict the sign of the NN interactions for the different positions along the chain. The second neighbor exchange has been considered to be anti-ferromagnetic in agreement with experimental results.

For the undoped Sr_{14}Cu_{24}O_{41} system we studied the two types of filling considered in the literature, namely with all the holes on the chains (fig. 4a1) and with one hole transfer per f.u. (fig. 4a2). When all the holes are on the chains, we retrieve a spin arrangement consistent with the experimental observations [8, 11, 13], that is dimeric units formed of two second neighbors spins, separated by two ZR singlets. These dimers are clustered by three or four units separated by a free spin, that is a spin with neither first nor second neighbor spin. We found 5 free spins for 100 sites (0.5 per f.u.) to be compared with the magnetic susceptibility measurements of 0.55 free spins per f.u. [14]. The number of dimers is 17 (1.7 per f.u.) to be compared with the magnetic susceptibility finding of 1.47 per f.u.. When one hole per f.u. is transfered to the ladders, the picture is totally modified. Indeed, the free spins totally vanish and first neighbor ferro-magnetically coupled spins appear. At the same time the number of (isolated) dimers is strongly reduced, with only 5 for 100 sites, that is 0.5 per f.u. From this analysis it is clear that if there are holes transferred to the ladders (at low temperature) in the undoped compound, this number is much smaller than 1 per f.u..

For the x = 13.6 doped system we studied three types of filling where n = 1, 2, or 3 holes have been transferred to the ladders. For all fillings, we retrieve arrangements with nearest neighbors spins and no second neighbors dimeric units. The chains are essentially composed of low-spin clusters (either in a singlet or doublet state), with spin arrangements that present weak exchange frustration. Such fillings are thus expected to be specially stable, and should be put into perspective with the anti-ferromagnetic ordering seen in magnetic susceptibility and ESR measurements. For n = 1, 2 one still observes a large number of free spins, while for n = 3 they have essentially disappeared, in agreement with magnetic susceptibility experiments [14].

In summary, we have studied the importance of the structural modulations on the low energy physics of the Sr_{14–x}Ca_{x}Cu_{24}O_{41} family. Surprisingly these distortions are not simply responsible for parameters distortions.
around their average value (except for the NN effective exchange on the undoped compound), but induce very large variations of the orbital energies, NN effective hopping and exchange. This is the variation of the OE (which spans a range of 1.2 eV for \( x = 0 \) and 2.2 eV for \( x = 13.6 \)) that is responsible for the low energy properties of the compounds, through the localization of the magnetic electrons. It is in particular responsible of the formation of dimers in the undoped compound. In view of these results one can also suppose that the stabilization of part of the chains sites by larger structural modulations, is responsible for the hole transfer toward the ladders in the doped compounds. In the \( x = 13.6 \) compound, the structural modulation is so large that it even reverse the sign of the NN effective exchange on part of bonds, lifting the exchange frustration that would arise for the large chain filling. In conclusion, one can say that the structural modulation is the key parameter, responsible for the large variation of the low energy properties in this family of compounds.

**Acknowledgment**: the authors thank Dr. D. Maynau for providing us with the CASDI suite of programs.

FIG. 4: 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 \( x = 13.6 \). The number of sites considered in both cases corresponds to a better approximation of the compounds unit cells than the 10/7 ratio, that is \( c_{ch}/c_{ta} = 3.9235/2.7268 \approx 100/69.5 \) for \( x = 0 \), and \( c_{ch}/c_{ta} = 3.90136/2.73607 \approx 77/54 \) for \( x = 13.6 \). Dots stand for ZR singlets, and the ellipsoids delimit spin clusters, which are magnetically very stable (with at most one second neighbor frustrated interaction).

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