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Evidences of stripe charge and spin ordering in $La_2NiO_{4+\delta}$ by electron spin resonance

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ABSTRACT

In order to study the effect of oxygen doping on magnetic correlations in La_2NiO_{4+d}, electron spin resonance (ESR) measurements, which allow to characterize the spin fluctuations, have been performed on three compounds with $\delta = 0.09$, 0.12, and 0.17. The ESR parameters anomalies are in relation with charge and spin order in stripes observed by others techniques such as neutron diffraction.

1. Introduction

The study of physical and structural properties of K_2NiF_4-type oxides has been a subject of great interest since the discovery of high temperature superconductivity in the cuprates $La_{2-x}Ba_xCuO_{4+\delta}$ (LBCO) [1] and $La_{2-x}Sr_xCuO_{4+\delta}$ (LSCO) [2]. The isostructural nickelate compound $La_{2-x}Sr_xNiO_{4+\delta}$ (LSNO) does not exhibit superconductivity at any value of doping (x or δ) [3], thus suggesting that copper may be playing a leading role in generating the superconducting state. On the other hand, both LSCO and LSNO exhibit a rich phase diagram, depending on the temperature and on the number of holes doped ($n_H = x+2\delta$) [4,5]. Even though both cuprates and nickelates have been extensively studied in the past, the spin dynamics and its connection with superconductivity in these materials remains unclear [6].

In both systems, LSCO [7,8] and LSNO [9], evidences of charge and spin order in stripes have been observed for some values of n_H. This order consists of lines of doped charges separating antiferromagnetic domains, and usually acting as anti-phase boundaries to the magnetic domains. In this state, the doped charges are ordered periodically, and are accompanied by spin-ordering. The oxygen non-stoichiometry or the chemical doping not only provide the charge for the stripes, but may also pin them [10–13].

While in the nickelate LSNO the stripe order is static [9], in the cuprate LSCO the stripes are dynamic [8], except when Sr is partially substituted by a rare-earth (Nd, Eu) [7] or by Ba [14]. In this case, the low-temperature tetragonal (LTT) phase becomes stable, and the resulting structural distortion acts to pin the stripes, thus rendering them static [12]. Recent data have shown that the bulk susceptibility in $La_{2-x}(Sr,Ba)_xCuO_4$ is dominated by the response of local moments due to the existence of spin-density-wave correlations [15]. For Ba doping with $x = 0.125$, a spontaneous symmetry breaking by stripe order has been observed [16]. The existence of static stripe order has also been observed in $La_{2-x-y}RE_ySr_xCuO_4$ by means of several different experimental techniques, such as neutron diffraction [6], muon spin relaxation [17], ARPES [18], X-ray scattering [19], and transport [20].

In spite of many studies, the mechanism of stripe formation, the link between the charge ordering organization in stripes for the nickelates and cuprates and the occurrence of superconductivity only in the cuprates are not understood and the dynamics of stripes remains a controversial subject [6,12].

In the present study, we focus on the nickelate system, which exhibits a more stable stripe order without the complication of superconductivity and allows us to investigate a large domain of doping with different techniques [9,10,21,22]. More specifically, we study the non-stoichiometric system $La_2NiO_{4+\delta}$ (LNO), in which the

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extra oxygen tends to order. This compound has been less studied than the (Sr) chemically doped system, where the dopants are randomly distributed (quenched disorder) [5,22]. The electron spin resonance (ESR) technique has been chosen due to its sensitivity to probe microscopic magnetic fluctuations. Moreover, this technique has already proven to be sensitive not only to magnetic, but also to charge ordering [23]. The Fig. 1 shows the schematic representations of LSNO and LNO tetragonal structure. For LNO, the intercalated oxygen statistically occupies either the position (¼¼ ¼) or the split position (¼ ¼ z) with $z \approx ¼$ for the space groups F4/mmm or Fmmm [24].

The La_2MO_4 (M = Cu, Ni) compounds are in general ESR silent; the absence of ESR signal is usually attributed to the two-dimensional (2D) magnetic fluctuations. Indeed, the relaxation processes may be so fast, that the signal broadens beyond the detection limit. Some authors have predicted by different models an observable ESR signal of Cu^{2+} species at high temperatures, above 600 K [25,26], but an ESR signal has never been detected up to 1150 K. Hence, the existing models, which only take into account the 2D antiferromagnetic (AF) fluctuations, cannot explain the experimental data. When the La_2MO_4 system is hole doped by introducing extra oxygen or Sr, an ESR signal can be detected. Sichelschmidt et al. [27] have observed in $La_{2-x}Sr_xCuO_{4+d}$ an ESR signal, the intensity of which varies in the same manner as the spin susceptibility, with a divergence at low temperatures. The authors concluded that the signal was due to the holes that are coupled with the Cu spins, thus leading to the formation of magnetic polarons. The appearance of magnetic polarons in the nickelate system has been predicted by Zaanen et al. [11] The spin-polaron or magnetic polaron state is a result of coupling the hole to the spin waves. This strong coupling leads to a polaronic character in the nickelate system and to a self trapping of charges. The stripes are oriented along the diagonal of the Ni square lattice, an alignment which is favored by the lattice distortions of the polaronic hole state [11,28].

Here, we use the ESR technique to systematically study the charge and spin fluctuations in oxygen doped nickelates, with the aim of getting an insight into the dynamics of the system. The intrinsic resonance signal of polycrystalline $La_2NiO_{4+\delta}$ samples with δ-values 0.09, 0.12 and 0.17 has been investigated in a large temperature range (10 K < T < 300 K). Phase separation of interstitial oxygen (Oi) was observed, leading to 1D or 3D oxygen ordering [28]. This phenomenon causes lattice distortions, which can pin the charge stripes. Similarly to the spin and charge ordering, the Oi order is described by a wave vector [29]. The $\delta = 0.12$ compound has been chosen as a starting point, since neutron diffraction studies at doping composition very close to this value [28] have well characterized the stripe order in this system, showing that the holes order at $T_{CO} \sim 200$ K, while the spins order at $T_S = 110$ K. This compound shows also a 3D oxygen ordering below $T_{oi} = 250$ K [9,29]. Site-centered and bond-centered stripe phases were observed for $\delta = 0.125$ [30,31]. The charge stripes are all oxygen centered for $T > T_S$, with a shift towards Ni centering for $T < T_S$. The bond-centered stripe configuration allows for the existence of a ferromagnetic component, resulting from the coupling of Ni^{2+} spins on either side of a domain wall in a straight line through a Ni^{3+} site. Then, a magnetic polaron is formed and a cooperative magnetic signal can be observed in ESR measurements.

By analogy, the ESR data on the $d = 0.12$ compound allowed us to interpret the results in the other two compounds. It has been shown by neutron diffraction studies [29] that the $d = 0.09$ compound exhibits a different interstitial oxygen ordering: the intercalated layers of oxygen are spaced periodically along the c axis, with a 1D ordering similar to the staging of intercalated graphite. In this compound, stripe order has never been reported. For the third composition, with $d = 0.17$, neutron diffraction studies on the charge and spin ordering in stripes have never been reported either, although NMR studies do indicate the existence of stripes close to 230 K. A spin freezing temperature of about 45 K is observed [32–34]. Furthermore, this last compound contains a number of holes ($n_H = 0.34$) very close to the LSNO compound with $x = 0.33$ ($n_H = 0.33$), where the stripe order has also been well characterized by neutron diffraction and the highest ordering

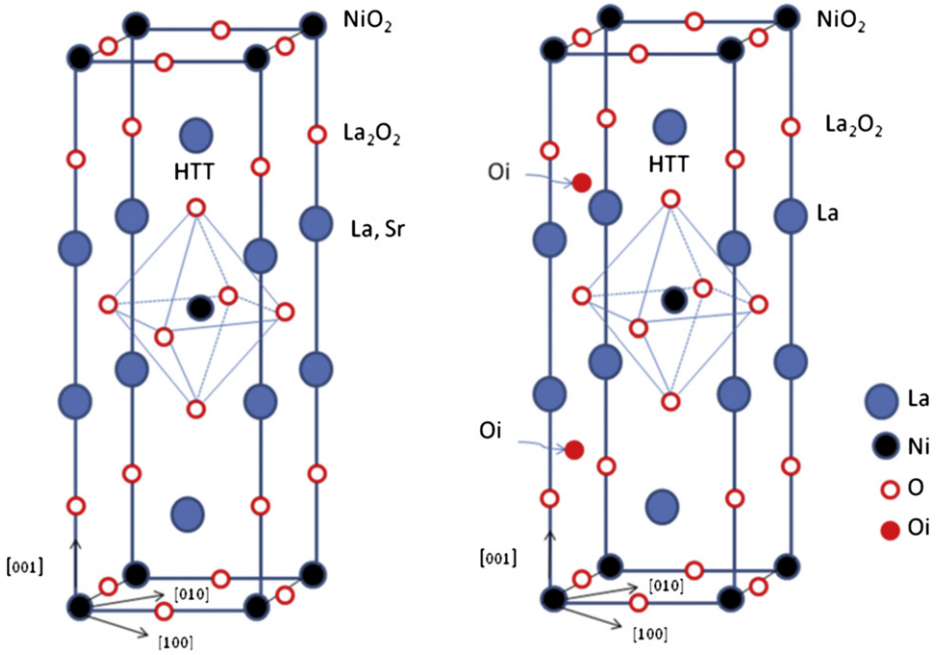

Fig. 1. Two schematic representations of K_2NiF_4 unit cell of HTT phase with lattice constants and basis vectors of $\sqrt{a} \times \sqrt{b} \times c$ supercell: (a) schematic structure of $La_{2-x}Sr_xNiO_4$, (b) schematic structure of $La_2NiO_{4+\delta}$.