Journal of Solid State Chemistry 220 (2014) 270–276

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Monoclinic distortion and magnetic coupling in the double perovskite $Sr_{2-x}Ca_xYRuO_6$

P.L. Bernardo [a], L. Ghivelder [a], G.G. Eslava [a], H.S. Amorim [a], I. Felner [b], S. Garcia [a,*]

[a] Instituto de Física, Universidade Federal do Rio de Janeiro, Cidade Universitária, Rio de Janeiro 21941-972, Brazil
[b] Racah Institute of Physics, The Hebrew University, 91904 Jerusalem, Israel

ARTICLE INFO

Article history:
Received 24 May 2014
Received in revised form
4 September 2014
Accepted 5 September 2014
Available online 16 September 2014

Keywords:
Double perovskites
Monoclinic distortions
Magnetic transition
$\pi-\sigma$ Mixing

ABSTRACTS

This work investigates in the insulating double perovskites $Sr_{2-x}Ca_xYRuO_6$. We address the angular dependence of the strength of the magnetic coupling due to the deviation from planarity of the basal layers of the monoclinic structure, characterized by the *in-plane* angle $\alpha<180^\circ$, in order to probe the impact of the structural distortions in the magnetic properties of the compounds. High resolution x-ray powder diffraction, susceptibility, and specific heat measurements were performed. The deviation from planarity significantly increases ($\alpha=144^\circ$ for $x=1$) while the bond distances vary in a complex way as a consequence of the strong monoclinic distortion. We found that the magnetic transition temperature, T_M, shows a linear dependence on cos $[(\pi-\alpha)/2]$. This result is discussed in terms of $t_{2g}(\pi)$–$e_g(\sigma)$ mixing of the magnetic orbitals of the Ru^{5+} ions and unbalanced competitive super-exchange interactions. The deleterious effect of Ca doping for the magnetic coupling is confirmed by the reduction in the short-range antiferromagnetic correlations characteristic of the parent compound at $T>>T_M$ and the enhancement of magnetic frustration for $T<T_M$.

1. Introduction

The compound Sr_2YRuO_6 belongs to the class of double perovskites with general formula $A_2BB'O_6$, where A=Ca, Sr, Ba and the B and B' sites are occupied by lanthanides, yttrium or 4*d*/5*d* transition metals [1]. All Ru ions are in the pentavalent state Ru^{5+} with octahedral oxygen coordination. In spite of this apparent simplicity, the magnetic and thermal responses exhibit a variety of very interesting features, previously described as anomalous [2]: a double peak in the magnetic contribution to the specific heat, a deviation from Curie–Weiss behavior, and a very low value of the change in magnetic entropy associated with the onset of long-range order and reduced magnetic moment in comparison to the expected value for a $^4A_{2g}$ $(J=3/2)$ high spin state, as determined from neutron powder diffraction measurements [3,4]. An understanding of these results was found through susceptibility, specific heat, thermal expansion and x-ray diffraction measurements [5]. It was shown that the magnetic and thermal responses are driven by the lattice changes, indicating that the interplay between the spin and structural degrees of freedom plays a crucial role in this compound. A distinctive feature characterizing the magnetic ground state is the delicate balance between ferromagnetic (FM) and antiferromagnetic (AF) interactions, where the sign and relative strength of the interaction between nearest and next-nearest Ru neighbors play an important role [6]. Long hybridization pathways, mediated by the $2p_{\pi,\sigma}$ oxygen orbitals, and the fact that the Ru ions form a face-centered cubic lattice are relevant for this balance, and is a classic example of geometric frustration [7]. On the other hand, the monoclinic distortion of the lattice, due to tilting of the RuO_6 octahedra, opens the possibility of Dzyaloshinskii–Moriya interaction [8], favoring a non-collinear spin state. Magnetic measurements in single crystals confirm the presence of weak ferromagnetism [9], while the temperature dependence of the coercive field H_C [2] evidence that the net FM moment shows a re-orientation in the vicinity of the magnetic transition and even a reversal in oxygen deficient samples [10]. All of these features support a scenario of a fine equilibrium of the magnetic ground state, which can be tuned by changing the structural parameters.

Of particular interest in this interplay is how the magnetic coupling depends on the deviation from planarity of the (Y,Ru)–(O_1,O_2) layers parallel to the ***a,b*** plane of the monoclinic structure, characterized by the bending angle $\alpha<180^\circ$. In general, this distortion is considered detrimental for magnetic interaction. However, there are some examples for which the magnetic transition temperature, T_M, rises as the deviation increases [11].

---

[*] Corresponding author. Tel.: +55 21 39387666; fax: +55 21 39387368.
E-mail address: sgg@if.ufrj.br (S. Garcia).

http://dx.doi.org/10.1016/j.jssc.2014.09.009
0022-4596/

This result shows that the specific features of each compound have to be considered to establish a reliable correlation. It has been proposed [12,13] that T_M correlates with the matrix elements V_{dpd} crossing the d- and p-states of the magnetic ions and oxygen, respectively. Although an explicit form of the V_{dpd} dependence on the interatomic distances was presented, a general description of the hybridization strength as a function of the bending angle was not provided. The exact functional form of the angular dependence of T_M is still an open issue. In this work, we conduct a detailed procedure to determine such dependence by studying the insulating $Sr_{2-x}Ca_xYRuO_6$ series of compounds with $x=0.0$, 0.2, 0.4, 0.6, 0.8 and 1.0. We found a linear dependence of T_M with $\cos\omega$, where $\omega=(\pi-\alpha)/2$. The results are discussed in terms of the effects of a crystalline field with monoclinic symmetry on the shift of the energy levels of the Ru^{5+} ions, which favor $t_{2g}(\pi)$–$e_g(\sigma)$ mixing of the magnetic orbitals. The width of the magnetic sub-bands derived from these levels was estimated and correlated with T_M. Contrary to the case of some metallic double perovskites [14], no correlation was detected, showing that the observed angular dependence is not associated with the kinetic terms in the Hamiltonian within the framework of hopping interactions.

2. Experimental

Polycrystalline samples of $Sr_{2-x}Ca_xYRuO_6$, with $x=0$, 0.2, 0.4, 0.6, 0.8 and 1.0, were prepared by conventional solid-state reaction with high purity $SrCO_3$ and $CaCO_3$ (BDH 99.99%), Y_2O_3 (LECO 99.99%) and RuO_2 (LECO 99.9% at least) powders. The initial mixtures were decomposed at 960 °C in air. After milling and pressing operations the material was sintered at 1060 °C for four days in oxygen flow, followed by cooling down to room temperature at a rate of 1 °C/min. High resolution X-ray powder diffraction (XPD) measurements at room temperature were conducted at the Brazilian Synchrotron Light Laboratory – LNLS. The sintered pellet was ground and sieved to reject grains larger than $\sim 5\ \mu m$. A wavelength of 1.7614 Å and 2Θ steps of 0.02° were employed. A Ge (1 1 1) crystal analyzer was used for detection. Rietveld refinement was carried out with the FULLPROF program. Field-cooled DC susceptibility measurements as a function of temperature were performed with a Cryogenic SX600 superconducting quantum interference device (SQUID) magnetometer, with an applied magnetic field $H=1$ T. The ceramic samples were cut in the form of long rods, to minimize demagnetization effects. They are placed in a plastic straw sample holder, in a way that only the sample itself contributes to the measured signal. The heat capacity measurements were carried out using a Quantum Design PPMS, in zero magnetic field at constant pressure, over a temperature range from 2 to 300 K using standard relaxation technique. The samples were cut in the form of small plates, with an area of the order of $3\times 3\ mm^2$, in order to fit within the platform of the calorimeter. The mass of the samples were around 20 mg. The heat capacity of the addenda and the grease used to provide thermal contact between the samples and the platform is measured separately and subtracted from the total measured heat capacity.

3. Results

The XPD patterns were refined using the monoclinic $P2_1/n$ space group for all samples. The profile fit achieved to the room temperature data for $x=0$, with no secondary phases, is given in Fig. 1 (top panel). The high resolution of the synchrotron XPD measurements allowed us to detect some remnant Y_2O_3, as shown in Fig. 1 for $x=0.2$ (bottom panel); this phase was also refined. Table 1 shows relevant lattice parameters and statistical fit values for the whole series. A stacked plot of the refinements for all the samples are given in Appendix A.

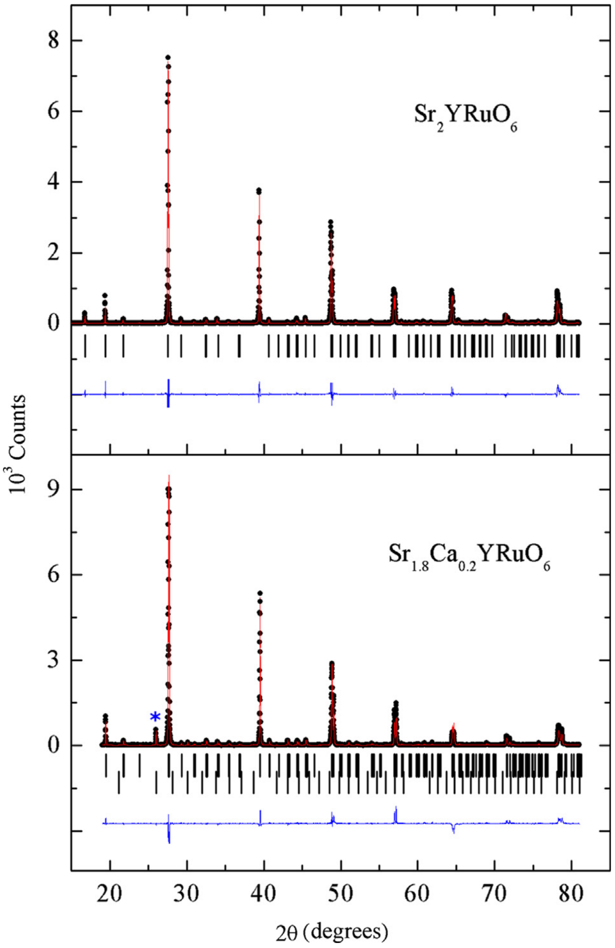

Fig. 1. High resolution X-ray diffraction patterns of Sr_2YRuO_6 and $Sr_{1.8}Ca_{0.2}YRuO_6$ measured at room temperature. The closed dots and solid lines represent observed and calculated patterns, respectively. The difference curve is shown at the bottom. Vertical bars indicate the expected Bragg peak positions. The asterisk indicates the strongest reflection for a remnant Y_2O_3 phase, which was also refined in the analysis.

The compositional dependence of the deduced lattice parameters a, b and c is presented in Fig. 2, showing a linear decrease with the increase in Ca content. The average bending angle α, between the Y and Ru ions in the (Y,Ru)–(O_1,O_2) layer, is calculated through the expression $\alpha=(\alpha_1+\alpha_2)/2$, where $\alpha_1=$Y–O_1–Ru and $\alpha_2=$Y–O_2–Ru are the *in-plane* angles, as shown in Fig. 3. The angle α decreases with the rise in x (inset, Fig. 2), exhibiting a significant departure from planarity ($\alpha=144°$ for $x=1$). The Y–O_3 (Ru–O_3) apical distance, also shown in Fig. 3, is enlarged (shortened) in the interval $0.2\leq x\leq 0.6$, followed by a reversal of this behavior for $0.6<x\leq 1.0$ (inset, Fig. 2). However, the Y–O_3 distance remains larger than the Ru–O_3 distance for all x values, keeping a typical characteristic of the parent compound due to the difference in valence between the Y^{3+} and Ru^{5+} ions. The average (Y,Ru)–O_3 distance diminish with the increase in x.

The temperature dependence of the susceptibility, $\chi(x,T)$, measured with $H=1$ T with a *field-cooled* procedure, is presented in Fig. 4 for all the studied samples. The peaks are shifted to lower temperatures and become broader with the increase in x. The inset of Fig. 4 shows the dependence of the magnetic transition temperature, $T_{M1}(x)$, taken as the maximum negative slope of the $\chi(x,T)$ peaks, on the average ionic radius at the A-sites, $\langle r_A\rangle$, exhibiting a decreasing behavior as $\langle r_A\rangle$ diminishes. Also shown in