

On the $\text{La}_{2-x}\text{Sr}_x\text{CoRuO}_6$ double perovskites: Crystal structure, magnetic properties and transport

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Abstract

As double perovskites have attracted attention due to the unusual magnetic properties and half-metallic nature of the charge carrier transport, the study of the $\text{La}_{2-x}\text{Sr}_x\text{CoRuO}_6$ perovskite offers a unique opportunity to examine the interplay of the cationic order, charge balance, transport and magnetic interactions between Co and Ru species. We confirm the existence of the B-site ordered double perovskite phase for $0.0 < x < 1.6$, whereas for higher x a single-phase perovskites with a statistical distribution of all cations is formed. Consistent picture of transport properties of B-site ordered perovskites with $x \sim 1$ is based on a supposition of the “ideal” valency of Co and Ru close to $2+$ and $5+$, respectively, when the real chemical composition leads to excess electrons ($x < 1$) or holes ($x > 1$). The magnetic data reveal that effective magnetic moment amounts $\sim 5.5 \mu_B$ and does not significantly vary with x . Weiss constant Θ_C , however, shows a parabolic-like dependence on x : from the antiferromagnetic $\Theta_C \sim -70$ K for $x = 0$, via a broad maximum for $x \sim 1.0$ with $\Theta_C \sim 15$ K and a decrease to $\Theta_C \sim -220$ K for $x = 2$. To explain this evolution we suggest that antiferromagnetic superexchange between Co and Ru ions is for $x \sim 1$ compensated by the reinforcement of ferromagnetic interactions, most likely associated with the formation of quasi-itinerant π^* bands (Ru–O).

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1. Introduction

Double perovskites have recently attracted attention due to the magnetic properties and half-metallic nature of the charge carrier transport [1,2]. In this respect, the study of the $\text{La}_{2-x}\text{Sr}_x\text{CoRuO}_6$ system offers a unique opportunity to examine the interplay of the cationic order, charge balance, transport and magnetic interactions between Co and Ru species coordinated in perovskite network. The recent studies of $\text{La}_2\text{CoRuO}_6$ and $\text{La}_{2-x}\text{Sr}_x\text{CoRuO}_6$ ($0.75 \leq x \leq 1.5$) [3,4] insinuated the complexity of magnetic interactions in these systems. The comprehensive study of $\text{La}_{2-x}\text{Sr}_x\text{CoRuO}_6$ ceramics ($0.0 \leq x \leq 2.0$) presented here analyze the composition limits of the existence of the B-site ordered double

perovskite phase, experimental data of magnetic and transport measurement between 4 and 800(1200) K enable to characterize magnetic interactions and analyze the nature of charge carriers. Finally, using the comparative analysis of experimental data, the valency of Co and Ru ions in conjunction with magnetic interactions and the mechanism of charge carrier transport are discussed.

2. Experimental

The ceramic samples of $\text{La}_{2-x}\text{Sr}_x\text{CoRuO}_6$ were prepared by solid state reaction. Stoichiometric amounts of SrCO_3 (99.9+%), La_2O_3 (99.9+%), Co_2O_3 (99.9+%) and RuO_2 (99.9+%) were mixed, homogenized in agate mortar and calcinated at 800 °C in air for 48 h. After regrinding the process was repeated at 850 °C and final powder was pressed into pellets, and heated for a total of 48 h at 1150 °C in air followed by slow cooling. The samples were characterized by X-ray powder diffraction at room temperature. The patterns were

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obtained using the X-ray diffractometer Bruker D8 and X-ray patterns were analyzed with the help of FULLPROF program package.

The magnetic susceptibility measurements in the temperature range 4–350 K were performed in applied field of 0.1 T on zero field cooled (ZFC) and on field-cooling (FC) ceramic samples. The magnetic experiments up to 350 K were performed using a SQUID magnetometer. In addition, high temperature susceptibility was measured up to 800 K using a pendulum magnetometer in an applied field of 1.8 T.

The thermoelectric power and electrical resistivity measurements were carried out using a home-made system within the temperature range 4–1200 K. The four point steady-state method with separated sensors and power contacts was applied, the principle and details of both low temperature (4–310 K) and high temperature (300–1200 K) measurements can be found e.g. in Ref. [5].

3. Results and discussion

The existence of perovskites' single-phase solid solutions for all x is confirmed by the linear variation of the unit cell volume with x – see upper panel of Fig. 1. The La and Sr ions are found to be distributed randomly for all x . The stability of the ordered double perovskite phase with $P2_1/n$ symmetry is determined within the composition region $x \in (0; 1.6)$. The degree of ordering is 80–90%, see lower panel of Fig. 1. The solid solutions with higher Sr concentration, i.e. $x \in (1.8; 2)$ are

simple perovskites with $I2/c$ symmetry and randomly distributed Co and Ru ions.

This experimental fact is in good agreement with the simple theoretical model supposing that the cobalt ions are for $x \in (0 \rightarrow 1)$ stabilized as Co^{2+} (Table 1). Simultaneously, due to the Sr for La substitution, the valency of Ru increases from $\text{Ru}^{4+} \rightarrow \text{Ru}^{5+}$ for $x \in (0 \rightarrow 1)$. In this respect we suppose that the ordered perovskite LaSrCoRuO_6 with Co^{2+} and Ru^{5+} ions, which differ significantly both by valency and size, represents an “archetype” for a perfectly ordered perovskite within this series. Due to increasing Sr substitution for $x \in (1 \rightarrow 2)$, the electrons are removed likely from Co ions leading to valency increase from $\text{Co}^{2+} \rightarrow \text{Co}^{3+}$, as Ru species are supposed to be already heavily oxidized. In coherence with the literature the Co^{3+} are supposed to adopt the high spin (HS, $t_{2g}^4 e_g^2$) or intermediate spin (IS, $t_{2g}^5 e_g^1$) rather than the low spin (LS, $t_{2g}^6 e_g^0$) state [6]. Consequently, the decreased charge and size difference between Ru^{5+} and Co^{3+} leads to formation of a simple perovskite structure. The above-mentioned hypothesis is visualised in Fig. 2, where the tolerance factor and absolute size difference between the Co and Ru ions is shown in dependence of x . The high difference of ionic radii between Co and Ru ions complemented by the difference in valency leads to the stabilization of the double perovskites while a small difference complemented by relaxed matching of A–O and B(B')–O bonds (tolerance factor $t \sim 1$) results in the stabilization of a simple perovskite.

The magnetic susceptibility reveals that the Co ions are in high or intermediate spin state and that together with Ru species form a complex magnetic structure as demonstrated by the temperature variation of the magnetic susceptibility measured between 5 and 800 K (Fig. 3). Analyzing the high temperature magnetism in $\text{La}_{2-x}\text{Sr}_x\text{CoRuO}_6$ we infer that magnetic interaction for all x are dominated by nearest neighbour interactions (NN) of superexchange type between HS/IS $\text{Co}^{2+,3+}$ and LS $\text{Ru}^{4+,5+}$ ions with prevailing antiferromagnetic character. It seems difficult to speculate whether the next nearest neighbour (NNN) magnetic interactions are important as well. The further surprising observation is that the effective magnetic moment does not vary with x . Its absolute value matches very well with expected valence distribution and Co spin state for $x=1$, i.e. HS Co^{2+} and Ru^{5+} ($\mu_{\text{theor}} = 5.48$). The constant μ_{eff} value in the $x \in (1; 2)$ region can be explained by a mixture of HS and IS states for Co^{3+} . This is in agreement with decreasing degree of site ordering with x , since Co^{3+} in HS state is only stable if it is surrounded by Co (or other cation) in LS state, whereas stabilization of Co^{3+} IS state is promoted by neighbours of the same kind [7]. The $\text{La}_2\text{CoRuO}_6$ is characterized by effective moment $\mu_{\text{eff}} = 5.45 \mu_B$ which can be understood supposing that significant positive contribution of orbital moment associated with Ru^{4+} ions reinforces the total μ_{eff} (a simple combination of Co^{2+} and Ru^{4+} without the orbital contribution leads to $\mu_{\text{eff}} = 4.8 \mu_B$).

The long range magnetic order of the $\text{La}_2\text{CoRuO}_6$ is characterized by Weiss constant $\Theta_C \sim -70$ K and clear antiferromagnetic transition at $T_N = 28$ K. For higher x the

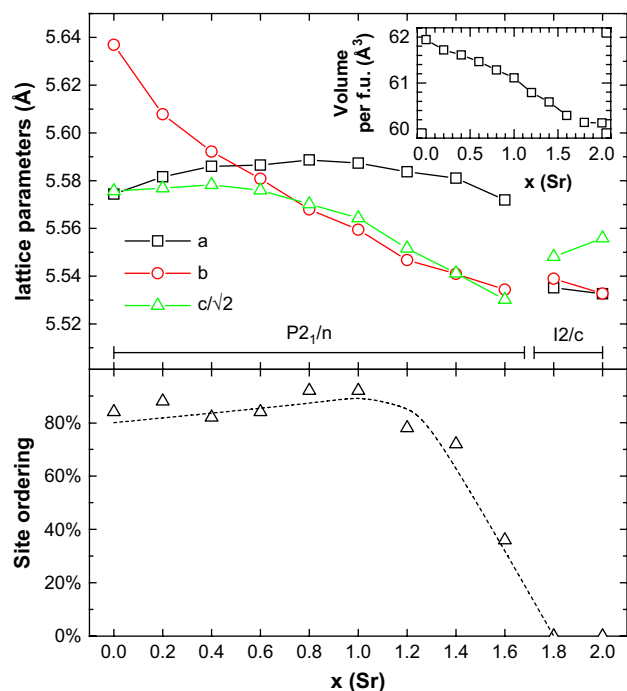


Fig. 1. Upper panel: composition dependence of lattice parameters for $\text{La}_{2-x}\text{Sr}_x\text{CoRuO}_6$. The inset shows the composition dependence of the unit cell volume. Error bars are smaller than symbol size. Lower panel: the composition dependence of B-site order in $\text{La}_{2-x}\text{Sr}_x\text{CoRuO}_6$. The dashed line is a guide for eyes.

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