



The impact of chemical doping on the magnetic state of the Sr₂YRuO₆ double perovskite



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ARTICLE INFO

Keywords:

Ruthenium perovskite
Crystal and magnetic structure
Rietveld refinement
Neutron diffraction

ABSTRACT

The impact of chemical doping of the type Sr_{2-x}A_xYRuO₆ (A=Ca, Ba) on the low temperature magnetic properties of Sr₂YRuO₆, probed using variable temperature magnetic susceptibility, neutron diffraction and heat capacity measurements, are described. Specific-heat measurements of un-doped Sr₂YRuO₆ reveal two features at ~26 and ~30 K. Neutron scattering measurements at these temperatures are consistent with a change from a 2D ordered state to the 3D type 1 AFM state. Magnetic and structural studies of a number of doped oxides are described that highlight the unique low temperature behavior of Sr₂YRuO₆ and demonstrate that doping destabilizes the intermediate 2D ordered state.

1. Introduction

Double perovskites A₂BB'O₆ with 1:1 rock salt like ordering can be described as having two interpenetrating face-centered-cubic sublattices, where the B and B' cations are located at the corners of an edge-sharing tetrahedral network [1]. In the particular case where a non-magnetic cation is located at one of the octahedral B-sites and a magnetic ion is on the other, long range nearest-neighbor antiferromagnetic interactions cannot be simultaneously established. Consequently, such a cation arrangement offers an excellent opportunity for the design of novel geometrically frustrated magnetic materials [2]. Such systems have been recently attracting considerable attention since they display a wide variety of exotic magnetic states including spin-liquids, spin-glasses and spin-ice [3,4]. The large number of competing ground states in geometrically frustrated magnets tends to destabilize magnetic ordering and may lead to remarkable correlated states at low temperatures.

The crystal symmetry of the double perovskite Sr₂YRuO₆, reported in 1984 by Battle and Macklin [5], is monoclinic (space group P₂₁/n), with the unit-cell parameters related with the ideal simple perovskite cell as a≈√2a₀, b≈√2a₀ and c≈2a₀, β≈90°, where a₀ is the edge of the primitive cubic ABO₃ perovskite. This superstructure is due to ordering of the Ru⁺⁵ (d³) and Y³⁺ (diamagnetic) cations over the two octahedral sites in combination with distortion of the oxygen sublattice. The latter can be described in terms of cooperative tilting of the three-dimensional network of corner sharing BO₆ octahedra [6,7]. In recent years, Sr₂YRuO₆ has aroused considerable interest aimed at explaining its anomalous magnetic behavior [8–10]. These include negative values of

the zero-field-cooled susceptibility curves, the presence of two low temperature transitions in the heat capacity measurements and the reduced value of ΔS_{mag}. To date a complete understanding of the magnetic properties of Sr₂YRuO₆ remains unclear.

Two recent studies by Granado et al. [11] and Bernardo et al. [12] have used neutron scattering to address our understanding of the unusual properties of Sr₂YRuO₆, however they proposed very different explanations. Granado concluded that the two features observed in the heat capacity arise due to changes from a 2D ordered state to the 3D type 1 AFM state whereas Bernardo *et al.* proposed a different K₂NiF₄-type magnetic structure and argued the two transitions are a consequence of spin reorientation of the net FM moment associated with a non-collinear spin configuration.

In the present contribution we firstly study the anomalous low temperature behavior of the perovskite Sr₂YRuO₆ by means of low temperature neutron powder diffraction, coupled with bulk susceptibility and heat capacity measurements. Having established the crystal and magnetic structures of undoped Sr₂YRuO₆ the influence of chemical doping in oxides of the type Sr_{2-x}A_xYRuO₆ (A=Ca, Ba) was investigated. The doped oxides were chosen to maintain the monoclinic P₂₁/n structure of the parent. Analysis shows that both larger and smaller cations destabilize the intermediate 2D ordered state seen in Sr₂YRuO₆.

2. Experimental

Approximately 10 g samples of Sr₂YRuO₆, Sr_{1.5}Ca_{0.5}YRuO₆, Sr_{1.5}Ba_{0.5}YRuO₆ and Sr_{1.75}Ba_{0.25}YRuO₆ were synthesized by solid state

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methods. Stoichiometric amounts of SrCO_3 , BaCO_3 , CaCO_3 , Y_2O_3 and Ru powder were grounded together in an agate mortar, placed in alumina crucibles and heated as follows: 12 h at 650 °C and 12 h at 850 °C with intermediate regrinding. After mixing again the powders were pressed into 20 mm pellets and heated in air at 1050 °C for 24 h, 1200 °C for 72 h and finally at 1400 °C for 72 h. The magnetic structure of Sr_2YRuO_6 at 5 K and its thermal evolution were determined from Neutron Powder Diffraction (NPD) data in the temperature range 5–75 K measured on the Echidna diffractometer [13] at ANSTO's Opal facility using neutrons of wavelength 2.44 Å. The NPD for the doped samples were measured at low temperatures using the same setup.

DC magnetic susceptibility data were collected under zero field cooled (ZFC) and field cooled (FC) conditions, using a Quantum Design Physical Properties Measurement System (PPMS), over the temperature range 4–300 K in a field of 1000 Oe using the vibrating sample magnetometer technique. Heat capacity measurements were collected from 4–100 K on the same platform using a thermal relaxation method. In order to estimate the magnetic heat capacity C_{mag} (T), the phononic and electronic contributions were subtracted from the total measured heat capacity by fitting a polynomial equation, $C_{\text{Lat}} = \sum_{n=0,1,2,\dots,5} A_n T^n$, for temperature intervals outside the region of interest.

3. Results and discussion

Fig. 1 shows the thermal evolution of the NPD patterns for Sr_2YRuO_6 in the range from 5 to 75 K. At 30 K the presence of additional low-angle reflections associated with the magnetic contribution to the scattering is observed, which is consistent with the onset of long-range antiferromagnetic ordering evident in the bulk susceptibility measurements. Although no long-range ordering magnetic peaks are observed above of 30 K, diffuse magnetic scattering persisted up to 75 K. Similar diffuse scattering was also observed in the recent study of Granado et al. [11], and has also been found in other double perovskites including Ba_2YRuO_6 [14] and $\text{La}_2\text{LiOsO}_6$ [15].

The crystal and magnetic structures below T_N were determined from the Rietveld analyses [16] of the NPD data, using the computer program Fullprof [17]. The plot of the observed and calculated profiles, including both the crystallographic and magnetic phases, is shown in Fig. 2a. Table 1 includes the most important refined parameters. All of the magnetic peaks were indexed with the propagation vector $\mathbf{k}=(000)$, thus the magnetic unit cell coincides with the chemical one. The propagation vector has been calculated using K_SEARCH in FullProf and the subsequent determination of the magnetic structure was accompanied using BasIrep as implemented in Fullprof [17]. Among the possible magnetic modes compatible with the space-group sym-

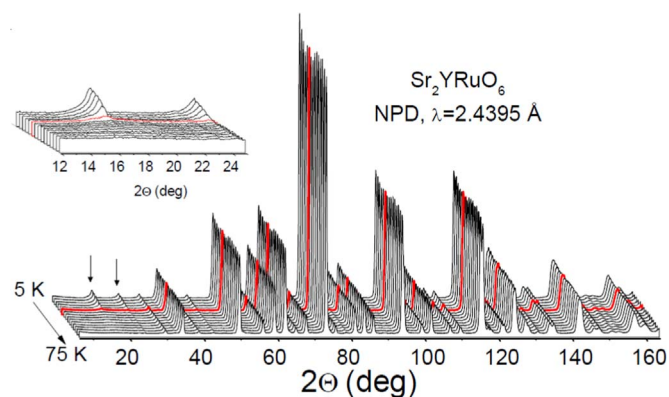


Fig. 1. Thermal evolution of the NPD patterns of Sr_2YRuO_6 , acquired with $\lambda=2.44$ Å in the temperature interval $5 < T < 75$ K. The pattern collected at 30 K is red colored to indicate the origin of additional peaks due to the coherent magnetic scattering. The inset shows a magnified portion in the $12 < 2\theta < 25$ region.

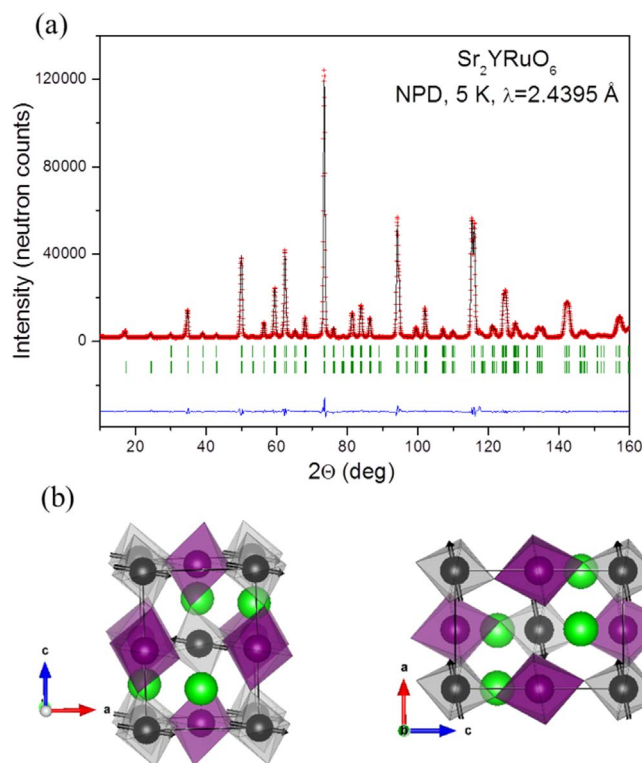


Fig. 2. (a) Observed (crosses), calculated (solid line) and difference (bottom) NPD Rietveld profiles for Sr_2YRuO_6 at 5 K collected at Echidna diffractometer (ANSTO). The upper and lower series of Bragg reflections correspond to the nuclear and magnetic phase respectively. (b) Schematic view of the magnetic structure of Sr_2YRuO_6 below T_N .

metry and this propagation vector, the best agreement with the experimental data was obtained for the magnetic structure where the $\text{Ru}_1(0,0,0)$ and $\text{Ru}_2(1/2,1/2,1/2)$ spins are magnetically coupled as $m_{1x}=-m_{2x}$, $m_{1y}=m_{2y}=0$, $m_{1z}=-m_{2z}$. The refined components of the magnetic moment along the crystallographic axes at 5 K are $m_x=2.16(2)$ μ_B and $m_z=-0.4(1)$ μ_B , and the net moment is $2.19(2)$ μ_B , which is consistent with the previously reported values of $1.85(10)$ μ_B [5] and 1.96 μ_B [11]. The moment reduction with respect to the theoretical magnetic moment, $3\mu_B$ ($S=3/2$) per Ru^{5+} , is likely due to covalency effects in the Ru–O bonds [5]. We also tested the $\mathbf{k}=\frac{1}{2}, \frac{1}{2}, 0$ propagation vector with the moments in the ab -plane, however this did not reproduce the magnetic intensity ratios and gave an unacceptably high $R_{\text{mag}}\sim 32\%$. Interestingly, the $\mathbf{k}=\frac{1}{2}, \frac{1}{2}, 0$ model with the moment along the c -axis produces very similar magnetic intensities to those of $\mathbf{k}=0,0,0$ ($R_{\text{mag}}=8.00\%$) with the moments in the ab -plane but the R_{mag} is still slightly higher (10%).

As shown in Fig. 2b, the magnetic structure consists of ferromagnetic (001) layers of Ru^{5+} moments coupled antiferromagnetically along [001], characteristic of a type-I Anti-Ferromagnetic Structure (AFM) structure, as originally identified by Battle and Macklin [5]. This model is different from that described recently by Bernardo et al. [12], a point we will return to below.

In order to correlate the NPD results with those obtained from heat capacity and magnetic susceptibility measurements, the temperature dependence of the spin orientation near the magnetic ordering temperatures was examined, Figs. 3 and 4. The magnetic susceptibilities of the samples was previously reported under both field cooled (FC) and zero-field cooled (ZFC) conditions in Ref 24. The data in the paramagnetic region were analysed using a linear Curie–Weiss fit from which the Weiss constant and the effective moment per formula unit were determined (Table 1–Ref 24). The negative Weiss temperature, $\theta=-273.54$ K, indicates that the predominant magnetic interactions are antiferromagnetic. The observed effective magnetic moment ($3.73\mu_B$)

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