Magnetic behavior of Sr_2DyRuO_6 complex perovskite

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The complex perovskite-type compounds Sr_2DyRuO_6 have been synthesized, and their crystal structures and magnetic properties have been reported. Powder X-ray diffraction measurements at room temperature and Rietveld analysis show that these compounds crystallizes in a monoclinic perovskite-type structure with $P2_1/n$ (#14) space group and the 1:1 ordered arrangement of Ru^{5+} and Dy^{3+} cations over the six-coordinate M sites. Results of fitting of the Curie-Weiss law to the curves of magnetic susceptibility as a function of temperature, performed by using the known zero field cooling (ZFC) and field cooling (FC) recipes, show that Sr_2DyRuO_6 exhibits an antiferromagnetic-like behavior at low temperatures, as a consequence of a magnetic transition at 38 K. Data collected of the field-dependence of the magnetization represented as a magnetic hysteresis loop, show the existence of a weak ferromagnetic moment relationship with the antiferromagnetic-like behavior

Keywords: X-ray diffraction; complex perovskite, structure; magnetic properties.

Se reporta la estructura cristalinas y las propiedades magnéticas del compuesto complejo tipo perovskita Sr_2DyRuO_6. Medidas de difraccion de rayos X a temperatura ambiente y análisis Rietveld muestran que el material cristaliza en una estructura monoclínica tipo perovskita perteneciente al grupo espacial $P2_1/n$ (#14) y presenta una disposicion ordenada 1:1 de los cationes de Ru^{5+} y Dy^{3+} en los seis sitios coordenados M. Los resultados del ajuste a la ley de Curie-Weiss de las curvas de susceptibilidad magnética en función de la temperatura, realizada mediante medidas ZFC y FC muestran que el compuesto Sr_2DyRuO_6 exhibe un comportamiento antiferromagnético a bajas temperaturas, como consecuencia de una transición magnética a 38 K. Los datos colectados de la dependencia del campo con la magnetizacion representada como un ciclo de histéresis magnética, muestran la existencia de un momento ferromagnetico relacionado con el comportamiento antiferromagnético.

Descriptores: Difracción de rayos X; perovskita compleja; estructura; propiedades magnéticas.

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1. Introduction

Complex perovskites have the general formula $A_2MM'O_6$, where A is an alkaline earth metal, M is a $3d$ transition metal and M' is a metal transition cation. These materials adopt a diverse range of structures and in function of the tolerance factor τ, the perovskites may have a simple cubic structure (τ=1), with space group $Pm-3m$ or can be distorted if $\tau > 1$ or $\tau < 1$, with lower symmetry [1]. On the other hand, double perovskites evidence a wide range of electronic properties and show a variety of magnetic behavior at low temperatures [2]. Currently, these materials have attracted special attention in advanced materials research due the presence of tunneling magnetoresistance at room temperature [3], and other properties such as high temperature superconductivity [4], colossal magnetoresistance [5], half-metallicity [6], and magnetoelectricity [7], besides several members of the double perovskite group can be considered for spintronics applications in industry [8]. Previous studies have shown that the double perovskites of the type Sr_2TbRuO_6 and Sr_2HoRuO_6 evidence antiferromagnetic ordering at $30-40K$, and the magnetic susceptibilities have a complex dependence with temperature below the transition temperatures [9]. In order to explain the magnetic behavior

of Sr_2DyRuO_6 complex perovskite, we report measurements of magnetic susceptibility as a function of temperature, performed by using the known zero field cooling (ZFC) and field cooling (FC) recipes. This double perovskite can be used as precursor oxide for the synthesis of $RuSr_2DyCu_2O_8$ by the solid-state reaction procedure. $RuSr_2DyCu_2O_8$ has been investigated because evidences coexistence of magnetic ordering and superconductivity at low temperatures [10], but the origin of magnetic behavior in the material $RuSr_2DyCu_2O_8$ is still discussed. In this work, we perform an experimental study of magnetic proprieties and analysis showing that Sr_2DyRuO_6 complex perovskite, behaves as an antiferromagnetic material.

2. Experimental

The ceramic sample of material Sr_2DyRuO_6 was prepared by solid-state reaction method from stoichiometric amounts of $SrCO_3$, RuO_2 and Dy_2O_3 (Aldrich 99.99%). To produce samples of 0.35 g. In order to obtain the pure crystallographic phase of Sr_2DyRuO_6 complex perovskite, the initial mixture was mixed in an agate mortar and pressed under a pressure of 2.3×10^{10} Pa to form cylindrical pallets of 4.9±0.1 mm
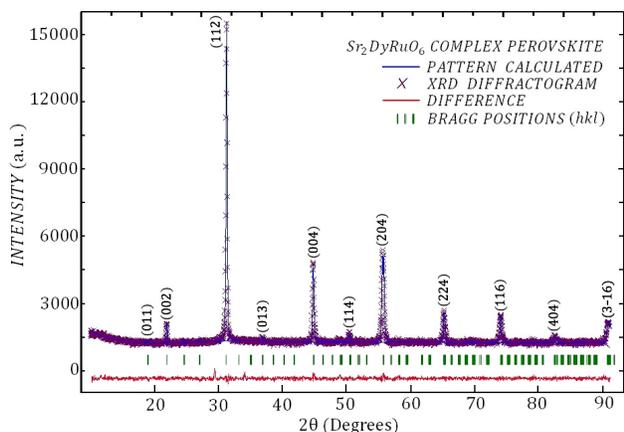
FIGURE 1. XRD pattern for Sr$_2$DyRuO$_6$ complex perovskite. Symbols correspond to the experimental data. The continuous line is the theoretical pattern obtained from Rietveld refinement. The bottom curve represents the difference between experimental and calculated patterns and the verticals green lines are the Bragg positions.

diameter and 1.2±0.1 mm thickness. These samples were then annealed at 1123 K for 12 h and sintered at 1253 K for 24 h, with frequent regrindings and repelletings. Structural characterization was performed through X-ray diffraction (XRD) measurements, in the region of $0° \leq 2\theta \leq 90°$, with the step size of 0.02°, using a Panalytical Xpert Pro diffractometer PW1710 with CuK$_\alpha$ =1,5406 Å radiation. A Rietveld refinement of diffraction pattern was carried out by means the GSAS code [11]. Refinement results were compared with characteristic values predicted by the Structure Prediction Diagnostic Software (SPuDs), which was created for perovskite-like materials [12]. In order to obtain the magnetic response of material, zero field cooling (ZFC) and field cooling (FC) measurements of magnetic susceptibility as a function of temperature, and magnetization as a function of applied magnetic field, were carried out by using an MPMS Quantum Design SQUID.

3. Structural results

Figure 1, shows the powder X-ray diffraction pattern for the Sr$_2$DyRuO$_6$ complex perovskite. In this, the continuous curve corresponds to the calculated pattern by means of the GSAS code, and the crosses represent the experimental data. The verticals short lines in the bottom of picture and the curve in red show the locations of Bragg peaks and the difference between the experimental pattern and the calculated one respectively.

The Rietveld refinement reveals that this compound has a monoclinic perovskite-type structure, which belongs to the space group P2$_1$/n (#14).The presence of (011), (013) and (114) peaks in the diffractogram of figure 1, confirms the existence of the superstructure that characterizes the double perovskites. The explanation of distortion from the ideal cubic perovskite structure is clear because the Sr$_2$DyRuO$_6$ com-

plex perovskite have the generic formula A$_2$M$'$M$''$O$_6$, and for this type of material the tolerance factor τ, is calculated by the ratio:

$$\tau = r_A + r_0/\sqrt{2}((r_{M'} + r_{M''}/2) + r_0), \qquad (1)$$

where r_A, $r_{M'}$, $r_{M''}$ and r_o are the ionic radii of the A, M', M'', and O ions, respectively. In agreement with the prediction of SPuDs program, the value of tolerance factor for the Sr$_2$DyRuO$_6$ complex perovskite is τ=0.9309. The structure present a distortion of the ideal cubic perovskite structure, because the Dy-O$_{6/2}$ and Ru-O$_{6/2}$ octahedral in Sr$_2$DyRuO$_6$, conserve the union between their corners while support the tilting of Dy-O$_{6/2}$ and Ru-O$_{6/2}$ octahedral, as a consequence of this, the material suffer a decrement in the symmetry. Then the Ru^{5+} and Dy^{3+} cations occupy two crystallographic independent octahedral sites, namely 2d and 2c [13]. On the other hand, the formation of a superstructure permit to establish the alternate distribution of the Ru^{+5} and Dy^{+3} ions on the six coordinate M sites of the perovskite, while the Sr^{2+} is located in the A-site, as show the Fig. 2.

The refined lattice and other important parameters determined from the Rietveld refinement are listed in Table I.

4. Magnetic properties

Figure 3, exemplifies the behavior of the magnetic susceptibility as a function of temperature for the Sr$_2$DyRuO$_6$ material. In the insets of Fig. 3, it is show that the maximum of the FC procedure was reached for $T = 20$ K. while the maximum of the ZFC recipe occurs for $T = 38$ K. The negative value of the magnetic susceptibility of the ZFC measure for temperatures below 34 K, shown in Fig. 3, is produced by the change in the orbital motion of electrons due to the applied magnetic field. This is because in the material induces a permanent magnetic
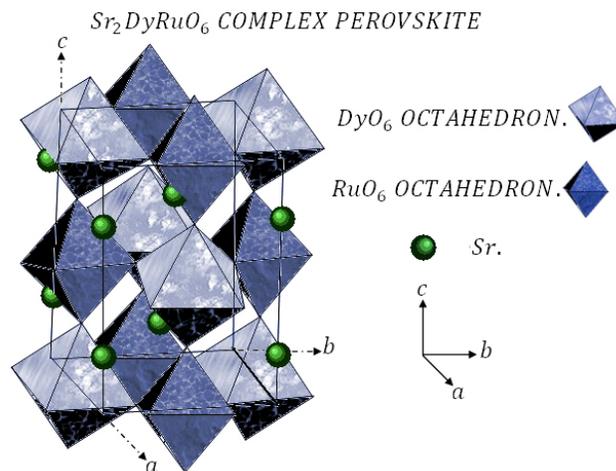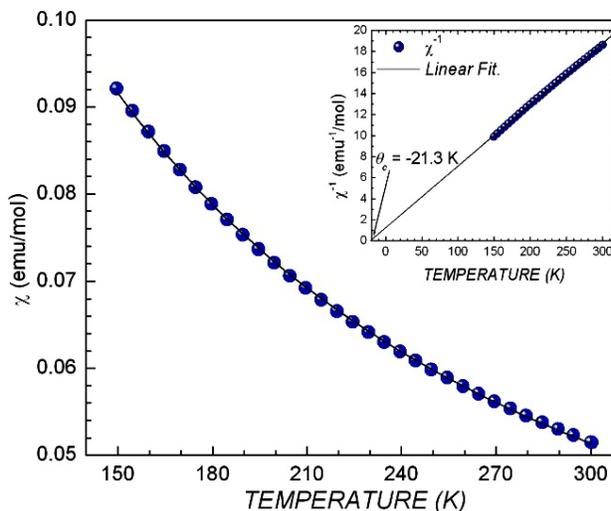

FIGURE 2. Crystal structure of Sr$_2$DyRuO$_6$ complex perovskite, the continuous lines in black indicate the primitive perovskite unit cell.

TABLE I. Structural parameters for Sr_2DyRuO_6 complex perovskite.

Space group: $P2_1/n$ (#14).

Unit cell parameters obtained from Rietveld refinement of X-Ray diffraction (XRD) pattern.

a=5.7774(2) Å, b=5.7948(2) Å, c=8.1848(2) Å, β=90.18(3)°, V=276.88(1) Å^3, τ=0.930(9)

Powder data statistics from Rietveld refinement.

$\chi^2 = 1.115$, R_F=5.8%, R_{wp}=3.87%, R_P=2.97%, R_e=3.41%.

Atomic positions obtained from XRD analysis.

Atom	Sr	Dy	Ru	O (1)	O (2)	O (3)
Site	4e	2c	2d	4e	4e	4e
x (Å)	0.50356(1)	0.0	0.5	0.22560(0)	0.31180(0)	0.41031(9)
y (Å)	0.51235(4)	0.5	0.0	0.19170(0)	0.72710(0)	0.98420(0)
z (Å)	0.25004(6)	0.0	0.0	0.95690(0)	0.95690(0)	0.23172(2)

Main inter-atomic distances and valences.

Cation	Anion	Multiplicity	Distance (Å)	Valence	Main bond angles (?).	
Dy (2C)	O (4e)	×2	2.240(1)	0.510(3)	Dy(2c)-O(4e) Ru(2d)	153.03(7)
Dy (2C)	O (4e)	×2	2.259(5)	0.500(0)	Dy(2c)-O(4e) Ru(2d)	152.64(2)
Dy (2C)	O (4e)	×2	2.256(4)	0.510(1)	Dy(2c)-O(4e)-Ru(2d)	151.02(3)
Ru (2d)	O (4e)	×2	1.950(7)	0.832(5)	O(1)-Dy-O(2)	91.41(3)
Ru (2d)	O (4e)	×2	1.966(8)	0.832(1)	O(2)-Dy-O(3)	90.29(4)
Ru (2d)	O (4e)	×2	1.969(8)	0.834(2)	O(3)-Dy-O(3)	88.58(8)
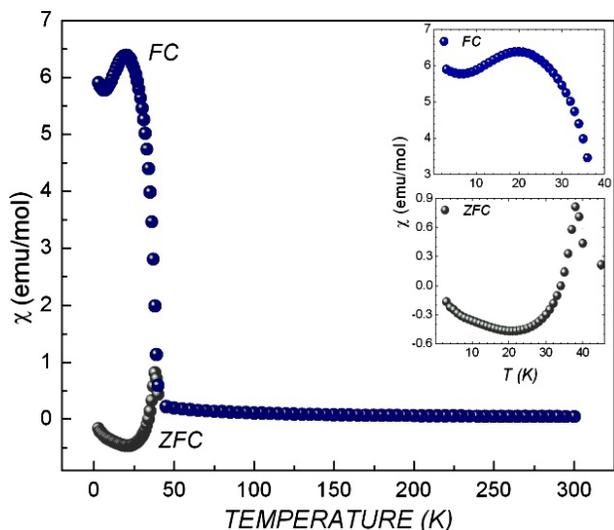
FIGURE 3. Measurements of susceptibility as a function of temperature for Sr_2DyRuO_6 on an applied field of H=5×10^{-4} T. In picture, the ZFC and FC procedures are specified.

FIGURE 4. Susceptibility as a function of temperature (circles) and Curie Weiss fitting (continuous line) for Sr_2DyRuO_6 material, the inset shows the Curie Weiss fitting on the inverse of susceptibility as a function of temperature.

magnetic moment of electrons and as the magnetic moment of an orbit, is proportional to its angular momentum, then by applying a magnetic field altering electronic movements and create an induced angular momentum with which the electron orbits around the nuclei are changed. As the currents induced by a magnetic field have such a sense that their magnetic field tends to oppose the original field. Then the magnitude of the induced magnetic moment is extremely small and in the op-

posite direction to the applied field. Which results in a negative magnetic susceptibility, associated with the diamagnetic term χ_o [14]. Besides this, there is a separation of the measures of ZFC and FC susceptibility at a temperature of 40 K. This indicates that at this temperature one transition of magnetic ordering occurs in the material. The paramagnetic behavior of Sr_2DyRuO_6 complex perovskite at high tempera-
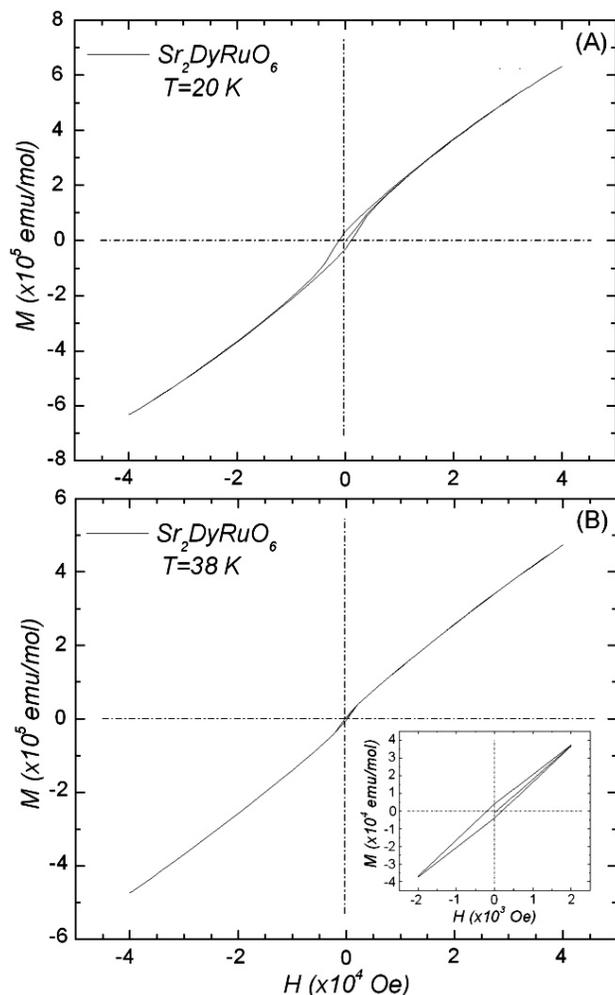
FIGURE 5. Magnetization as a function of field (continuous line) for Sr$_2$DyRuO$_6$ complex perovskite, at (A) 20 K and (B) 38 K

atures is due to the small contributions of magnetic moment of Ru^{5+} ion and the considerable contribution of the Dy^{3+} ion.

The fitting of the experimental data from the Curie-Weiss law $\chi = \chi_0 + C/(T + T_N)$ for temperatures in the range of $150 \ K < T < 300$ K, is shown in the Fig. 4. The obtained results reveal that Sr$_2$DyRuO$_6$ complex perovskite, behaves as an antiferromagnetic material below a Néel temperature $T_N = 21.3$ K (error 3.8%). This same fitting allow to determine the Curie constant C=13.065 emu.K/mol (error 3%), the temperature independent susceptibility χ_o=0.0053 emu/mol (error 2.5%), and the effective magnetic moment $P_{\rm eff} \ \mu_B$=11.67μ_B(error 6.4%). Theoretical calculations by the Hund's rule, with $P_{\rm eff}$=$g\sqrt{J(J+1)}$, predict that the magnetic moments of the isolated ions of Dy^{3+} and Ru^{5+} must be μ_{Dy}^{3+}=10.63 μ_B and μ_{Ru}^{5+}=3.87μ_B, respectively [15]. The effective magnetic moment of Sr$_2$DyRuO$_6$ is obtained to be $\mu_{\rm eff}$=11.31 μ_B(error 8%), where we have used:

$$\mu_{\rm eff} = \sqrt{\mu_{Dy^{3+}}^2 + \mu_{Ru^{5+}}^2} \qquad (2)$$

Below T_N it is observed that the antiferromagnetic ordering becomes to orientate spins anti-parallel to the applied field direction and the magnetic susceptibility decreases besides the magnetic ions in this compound may be affected by the crystal field to some extent. Divergence in measures ZFC and FC susceptibility at a temperature of 40 K suggests that Sr$_2$DyRuO$_6$ are not ideal antiferromagnetic material. This should be due to the contribution of the weak ferromagnetic component to the magnetic properties [2].

This explains the increase in FC susceptibility for temperatures below 10 K, because the total magnetic moment of the material is affected by the crystal field contribution. An analysis of magnetic hysteresis curves for temperature, to 20 K and 38 K, are plotted in Fig. 5. Results show that the value of the magnetization is greater for 20 K, because at this temperature the magnetic moments are oriented in the same direction. This magnetic hysteresis curve confirms the existence of an effective magnetic moment ordering in the material, and suggests that material behaves as an antiferromagnetic, but evidence effective magnetization at low temperatures due to the presence of magnetic clusters.

5. Conclusions

In this work we were carried out a study of the crystal structures and magnetic properties of Sr$_2$DyRuO$_6$ complex perovskite, prepared by solid-state reaction method. Results of Rietveld refinement showed that this compounds have a perovskite type structure, which is monoclinic with space group P2$_1$/n (#14). Fitting of the Curie-Weiss law to the curves of magnetic susceptibility as a function of temperature, showed that Sr$_2$DyRuO$_6$ exhibits an antiferromagnetic-like behavior at low temperatures, as a consequence of a magnetic transition at 38 K. With Néel temperature $T_N = 21.3$ K, Curie constant, $C = 13.065$ K temperature independent susceptibility χ_o=0.0053 emu/mol and the effective magnetic moment $P_{\rm eff}\mu_B$=11.67 μ_B. The magnetic hysteresis loop showed the existence of a weak ferromagnetic moment associated with the antiferromagnetism Due to the contribution of the weak ferromagnetic component to the magnetic properties the Sr$_2$DyRuO$_6$isn't ideal antiferromagnetic material.

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