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The Structure and Properties of β-La_3RuO_7: A New Structure Type with Isolated RuO_6 Octahedra

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A second lanthanum ruthenium oxide with the formula La_3RuO_7 is reported. This compound, β-La_3RuO_7, crystallizes in the $P2_1/c$ space group with a unit cell of $a = 8.8388(3)$ Å, $b = 5.6960(1)$ Å, $c = 12.5830(3)$ Å, and $\beta = 104.729(1)^\circ$, as refined from powder neutron diffraction data. The two major structural motifs in this structure are isolated RuO_6 octahedra and edge-sharing chains of OLa_4 tetrahedra. Magnetic susceptibility measurements show this compound to have a magnetic moment of $\mu_{eff} = 3.92\,\mu_B$ and a Weiss constant of $\theta = -70$ K. © 2002 Elsevier Science (USA)

INTRODUCTION

The Ln_3MO_7 [Ln = La–Lu, Y; M = Sb (1), Ta (1), Nb (2), Mo (3), Re (4), Ru (5), Rh (6)] family of quasi-1D materials contains corner-sharing chains of MO_6 octahedra, making them good candidate materials for the study of low-dimensional magnetism. The magnetic properties of this family are also interesting because this structure type exists for a wide range of d-electron counts, from d^0 to d^4, giving rise to chains with local moments that range from $S = 0$ through $\frac{3}{2}$. The subset of compounds with M = Ru (d^3) are the only members of this family to have the maximum transition metal low-spin local moment of $S = \frac{3}{2}$. Among the subset of d^3 Ln_3RuO_7 compounds, α-La_3RuO_7 is the only known compound with a nonmagnetic rare earth, providing a chance to study the physics of a $S = \frac{3}{2}$ chain within a nonmagnetic matrix.

Unfortunately, α-La_3RuO_7 is the most challenging member of the known Ln_3RuO_7 compounds to synthesize. Although this compound was originally reported to be impossible to synthesize (6, 7), later work showed that it is possible to make this compound using a precursor lanthanum ruthenate with an unknown composition and structure (8, 9). Here, we report the crystal structure and magnetic behavior of this precursor compound, β-La_3RuO_7.

Although the initial interest in β-La_3RuO_7 involved its value as a synthetic precursor for making α-La_3RuO_7, the antiferromagnetic behavior of β-La_3RuO_7 provides a valuable opportunity for understanding the magnetism of highly oxidized Ru compounds with isolated octahedra. Two other lanthanum ruthenates are known to have isolated RuO_6 octahedra, $La_{4.87}Ru_2O_{12}$ and $La_7Ru_3O_{18}$ (10). However, their RuO_6 octahedra are arranged in a geometrical array conducive to geometric frustration. The measured magnetic behavior of β-La_3RuO_7 provides a baseline for understanding the magnetism of highly oxidized Ru states in the absence of complicating geometric frustration, allowing the magnetism of the frustrated compounds $La_{4.87}Ru_2O_{12}$ and $La_7Ru_3O_{18}$ to be put in perspective.

EXPERIMENTAL

Powder samples were prepared by mixing dried La_2O_3 and RuO_2 in a 3.33:1 ratio of La:Ru. The well-ground mixture was placed in a dense Al_2O_3 and fired in air at 1000°C for 1 day and was further heated in air at 1100°C for few days with multiple regrindings. The reaction was judged complete when there were no longer any $La_{4.87}Ru_2O_{12}$ X-ray diffraction peaks (10) present. It was found that in air, 1100°C was the highest temperature that β-La_3RuO_7 could be prepared without decomposing into other lanthanum ruthenates, while the synthesis of α-La_3RuO_7 required a temperature of 1250°C and 1 atm of O_2 to prevent the formation of other lanthanum ruthenates. At intermediate temperatures, a mixture of the two phases was present. Although tiny single crystals of β-La_3RuO_7 could be obtained from crystal growths in salt fluxes (NaCl, KCl), these crystals diffracted too weakly to allow an accurate structure determination to be made. Nonetheless, unit cell and space group information ($P2_1/c$), and the approximate atomic

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parameters could be obtained using long exposure times (120 s/deg). These approximate values were used as the initial input for neutron diffraction refinements. Both field-cooled and zero-field-cooled magnetic susceptibility measurements were performed on powder samples of β-La_3RuO_7 using a Physical Property Measurement System (Quantum Design).

Powder neutron diffraction data were collected at the NIST Center for Neutron Research using the BT-1 32-counter high-resolution powder diffractometer. Room temperature data were collected using neutrons of wavelength 1.5401 Å produced by a Cu (311) monochromator. Collimators with horizontal divergences of 15′, 20′, and 7′ of arc full-width at half-maximum were used before and after the monochromator, and after the samples, respectively. Intensities were measured in steps of 0.05° in the 2θ range 3–168°. The lattice parameters were determined using GSAS (11) on data collected at 298 K. The neutron scattering amplitudes used in all calculations were $b(\mathrm{La}) = 0.827$, $b(\mathrm{Ru}) = 0.721$, and $b(\mathrm{O}) = 0.581$ ($\times 10^{-12}$ cm).

RESULTS AND DISCUSSION

Neutron diffraction data (collected on a ~ 10 g powder sample) were used to refine the structure of β-La_3RuO_7 in the monoclinic space group $P2_1/c$ (no. 14) with a unit cell of 8.8388(2) Å × 5.6960(1) Å × 12.5830(3) Å and $\beta = 104.729(1)°$. Structural parameters at room temperature are listed in Tables 1 and 2. The final three-phase refinement took into account the presence of two impurity phases (7.8 wt% La_2O_3 and 3.2 wt% α-La_3RuO_7) in addition to the majority phase (89.0 wt% β-La_3RuO_7). The calculated χ^2 (0.985) refined to a value less than 1 due to the underestimation of experimental errors, a problem that may occur when samples smaller than the instrumental norm (~ 20 g) are studied. The observed intensities, calculated intensities, and their difference are shown in Fig. 1.

An examination of the structure of β-La_3RuO_7 shows the two major structural motifs to be isolated RuO_6 octahedra and chains of edge-sharing OLa_4 tetrahedra. The connectivity of these chains, which run parallel to the b-axis, is readily seen when β-La_3RuO_7 is viewed along the a-axis (Fig. 2). The separation of these structural motifs is best seen in views along the b-axis (Fig. 3). Two-thirds of the La atoms (La2 and La3) are found in OLa_4 tetrahedra, while the other third of the La atoms (La1) only coordinate oxygens that are part of RuO_6 octahedra. Taking a cutoff of 3.2 Å as the upper limit for the La–O bond length, we find that all three La sites are nine-coordinate, and that all three La coordination polyhedra are quite irregular. The La–O bond distances in this structure are given in Table 3. It is interesting to note that the four shortest La–O bonds in the entire structure are found in the OLa_4 tetrahedron. The OLa_4 tetrahedra are quite regular, as all angles are within 10° of the 109.5° expected for an ideal tetrahedron. The isolated RuO_6 octahedra have no abnormal distortions. The O–Ru–O

TABLE 1
Crystal Data at Room Temperature

Formula sum	La_3RuO_7
Formula weight	2519.173
Crystal system	Monoclinic
Space group	$P2_1/c$ (no. 14)
Unit-cell dimensions (at 298 K)	$a = 8.8388(2)$ Å
	$b = 5.6960(1)$ Å
	$c = 12.5830(3)$ Å
	$\beta = 104.729(1)$
Cell volume	612.68(4) Å^3
Density, calculated	6.828 g/cm^3
R_p	3.81%
R_{wp}	3.09%
χ^2	0.985

TABLE 2
Atomic Coordinates and Thermal Parameters

Atom	Wyck.	X	Y	Z	$100U_{iso}$
La1	4e	− 0.0022(2)	0.0217(4)	0.1400(1)	0.75
La2	4e	0.2970(2)	0.0180(4)	0.4273(1)	0.67
La3	4e	0.4307(2)	− 0.0089(4)	0.1331(1)	0.60
Ru	4e	− 0.2143(3)	0.0434(4)	0.3333(2)	0.83
O1	4e	− 0.2511(4)	− 0.1256(5)	0.1969(3)	1.35
O2	4e	0.0079(4)	0.0567(5)	0.3328(2)	1.16
O3	4e	− 0.1700(4)	0.2654(6)	0.4658(2)	0.71
O4	4e	− 0.4328(3)	0.0440(5)	0.3262(2)	0.74
O5	4e	− 0.2385(4)	0.3416(5)	0.2528(3)	1.18
O6	4e	− 0.1891(4)	− 0.2410(5)	0.4273(2)	1.04
O7	4e	0.4917(4)	− 0.2625(5)	0.4897(2)	0.66

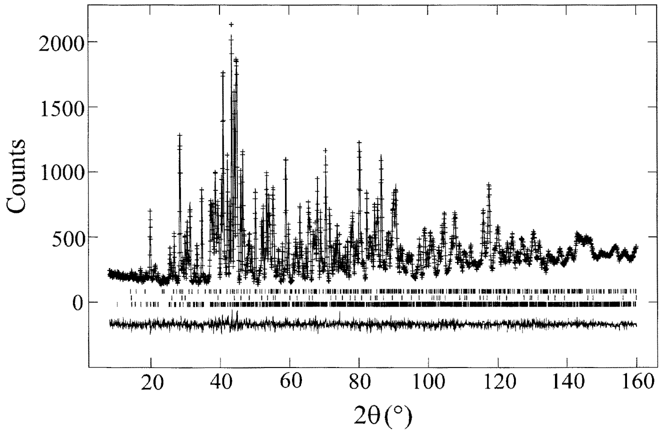

FIG. 1. Observed and calculated powder neutron diffraction pattern for β-La_3RuO_7 (89.0 wt%), La_2O_3 (7.8 wt%), and α-La_3RuO_7 (3.2 wt%) at room temperature. Below the observed data (crosses) and calculated (solid line) pattern, the difference plot is shown. Vertical lines indicate the Bragg reflection positions for β-La_3RuO_7 (bottom), La_2O_3 (middle), and α-La_3RuO_7 (top).

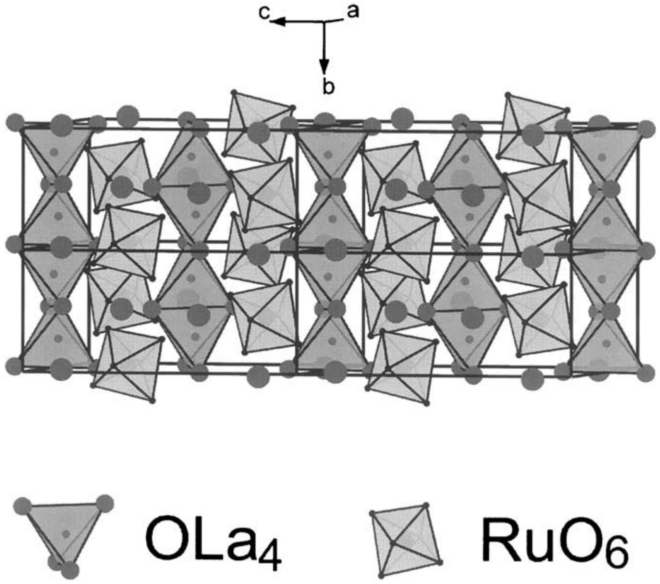

FIG. 2. Structure of β-La_3RuO_7 viewed nearly parallel to the *a*-axis, showing the isolated RuO_6 octahedra and the edge-sharing chains of OLa_4 tetrahedra. The RuO_6 octahedra are shown in light gray while OLa_4 tetrahedra are shown in dark gray. Oxygen atoms are represented as small black spheres, while La atoms are shown as large gray spheres. Ru atoms (medium spheres) are only found at the center of RuO_6 octahedra.

bond angles fall between 86 and 95°, and the Ru–O bond lengths ranging from 1.91 to 2.05 Å.

We briefly note that there is no simple distortion that will effect the transformation between β-La_3RuO_7 and α-La_3RuO_7. This is perhaps best seen in the two different connectivities of the OLa_4 tetrahedral networks. In addition to having the same stoichiometry and the same Ru^{5+} oxidation state, both compounds also have four formula units per unit cell. The smaller cell volume of β-La_3RuO_7 (612.7 vs 636.3 $Å^3$ for α-La_3RuO_7) means that this low-temperature structure type is about 4% denser than α-La_3RuO_7. The previously observed transformation from β-La_3RuO_7 to α-La_3RuO_7 on heating (8, 9) is believed to be more a result of chemical similarity than structural similarity.

In the two other lanthanum ruthenates with isolated RuO_6 octahedra, $La_{4.87}Ru_2O_{12}$ and $La_7Ru_3O_{18}$ (10), the RuO_6 octahedra are arranged around perfect or near-perfect three-fold rotation axes, leading to geometrical frustration of antiferromagnetic ordering. However, the spatial arrangement of octahedra in β-La_3RuO_7 seems to be very irregular. This absence of geometric order may allow β-La_3RuO_7 to serve as a benchmark for the unfrustrated magnetism of ruthenates.

A plot of the inverse magnetic susceptibility of β-La_3RuO_7 ($H = 1.0$ T) shows that Curie–Weiss behavior persists down to about 40 K (Fig. 4). A magnetic moment of $\mu = 3.92\,\mu_B$ and a Weiss constant of $\theta = -70$ K are obtained from the fit parameters after correcting for the presence of 7.8 wt% nonmagnetic impurities (La_2O_3). No correction was made for the presence of 3.2 wt% α-La_3RuO_7 due to its small volume fraction and its nearly identical magnetic moment. The moment of β-La_3RuO_7 is very close to the ideal moment of 3.87 μ_B for Ru^{5+} ions ($S = \frac{3}{2}$). As expected, the Weiss constant is very similar to the values found for $La_{4.87}Ru_2O_{12}$ (-85 K) and $La_7Ru_3O_{18}$ (-58 K), which also have isolated RuO_6

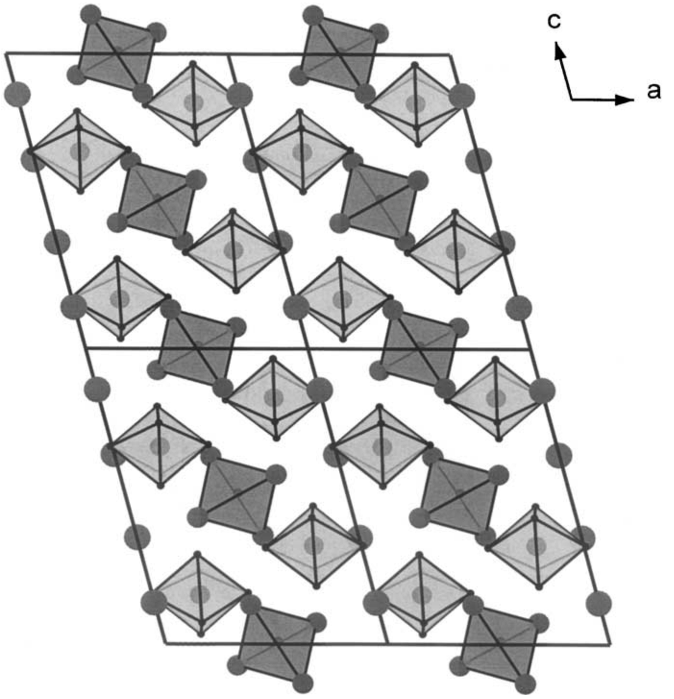

FIG. 3. Structure of β-La_3RuO_7 viewed parallel to the *b*-axis. The separation between the OLa_4 chains (which run parallel to *b*) can be clearly observed. It can also be seen that one axis of the RuO_6 octahedra is nearly parallel to the *a*-axis. Atomic and polyhedral representations are the same as in Fig. 2.

TABLE 3
Selected Bond Distances (Å)

Ru–O4	1.910(4)	La1–O6	2.476(4)	La2–O3	2.539(4)
Ru–O1	1.922(4)	La1–O3	2.611(4)	La2–O6	2.600(4)
Ru–O5	1.962(4)	La1–O1	2.619(4)	La2–O4	2.981(3)
Ru–O2	1.967(4)	La1–O2	2.673(4)	La2–O4	3.049(3)
Ru–O6	1.984(4)	La1–O3	2.692(4)		
Ru–O3	2.049(4)	La1–O2	3.068(4)	La3–O7	2.317(4)
		La1–O6	3.194(4)	La3–O7	2.395(4)
O7–La3	2.317(4)			La3–O4	2.442(3)
O7–La2	2.333(4)	La2–O7	2.333(4)	La3–O6	2.576(4)
O7–La2	2.351(4)	La2–O7	2.351(4)	La3–O4	2.597(4)
O7–La3	2.395(4)	La2–O5	2.411(4)	La3–O5	2.630(4)
		La2–O1	2.531(4)	La3–O3	2.655(4)
La1–O2	2.414(3)	La2–O1	2.539(3)	La3–O1	2.802(4)
La1–O5	2.437(4)			La3–O4	3.190(4)

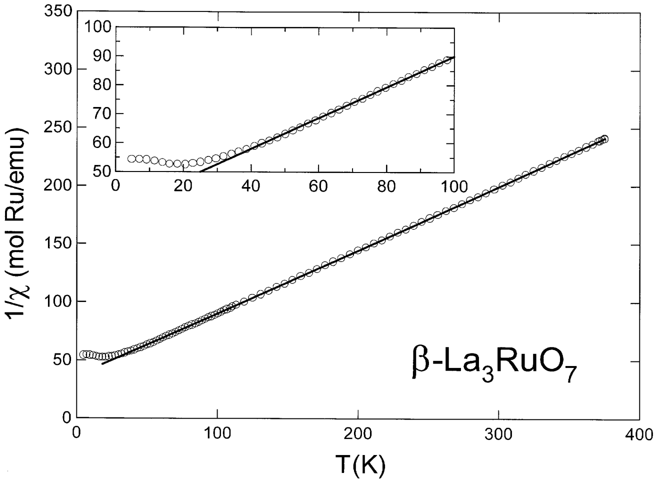

FIG. 4. Inverse magnetic susceptibility of β-La_3RuO_7 at $H = 1.0$ T. Solid line shows the fit to a Curie–Weiss law. Inset: zoom of the low-temperature regime.

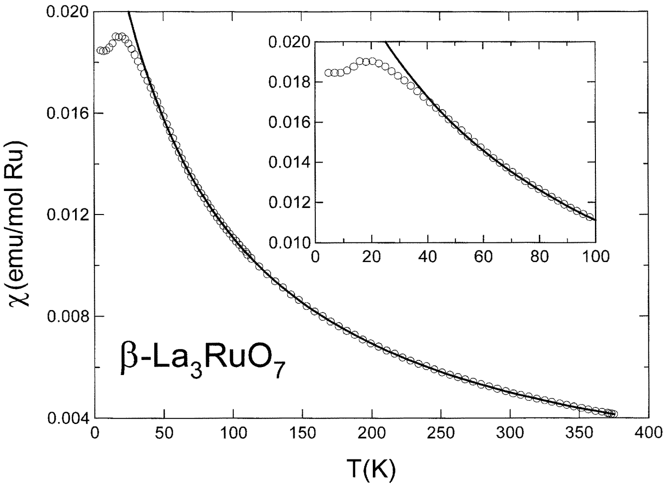

FIG. 5. Magnetic susceptibility of β-La_3RuO_7 at $H = 1.0$ T. Solid line shows the fit to a Curie–Weiss law. Inset: zoom of the low-temperature regime.

octahedra. Upon cooling below 18 K, β-La_3RuO_7 undergoes an antiferromagnetic ordering transition, seen as a peak in the magnetic susceptibility data (Fig. 5). The temperature of this transition is noticeably higher than the corresponding transitions in $La_{4.87}Ru_2O_{12}$ (4.5 K) and $La_7Ru_3O_{18}$ (14 K). Although $La_7Ru_3O_{18}$ appears to have a rich magnetic phase diagram, the behavior of β-La_3RuO_7 is consistent with a virtually field-independent antiferromagnetic ordering transition. We note that identical behavior was obtained with zero-field cooling using a 0.1 T field and with field cooling under a 1.0 T field.

CONCLUSIONS

The structure and magnetic properties of β-La_3RuO_7 have been characterized. The stoichiometry and Ru oxidation state have been found to be identical to those of the quasi-1D material, α-La_3RuO_7, making this new material an appropriate synthetic precursor for the α phase. The strength of the magnetic interactions in β-La_3RuO_7 are observed to be comparable to those of other lanthanum ruthenates with isolated octahedra, though the antiferromagnetic ordering temperature of β-La_3RuO_7 is the highest to date among these compounds.

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