

Magnetic Properties of the Fluorite-Related La_3MO_7 Phases, $M=\text{Ru}$ and Os

Local Moment Magnetism, Short- and Long-Range Order in $4d$ and $5d$ Transition Metal Oxides

Robert Lam, Frederick Wiss, and John E. Greedan¹

Brockhouse Institute for Materials Research, Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

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The oxide materials La_3MO_7 , $M=\text{Ru}$ and Os have been prepared, the Os phase for the first time. Both crystallize in a fluorite-related supercell with $Cmcm$ symmetry with very similar lattice constants. A singular feature of this structure type is the presence of well-separated zig-zag chains of corner-sharing MO_6 octahedra parallel to one of the orthorhombic axes. Local moment magnetic behavior is observed for both on very different energy scales. In each case the materials exhibit Curie–Weiss paramagnetism at high temperatures with effective moments consistent with $S = \frac{3}{2}$, as expected for the $4d^3$ and $5d^3$ electronic configurations associated with oxidation state +5, thus providing evidence for local moment magnetism. At lower temperatures broad maxima occur near 20 K (Ru) and 110 K (Os) which can be attributed to intrachain magnetic correlations. Fits to an appropriate model yield J^{intra}/k values of -2.9 K for Ru and $-23.2(1)$ K for Os . This \sim eight-fold increase is attributed to the expanded radial extent of the d -orbitals in proceeding from the $4d$ to the $5d$ series. Evidence for long-range antiferromagnetic order is present in the form of sharp susceptibility maxima at 10 and 45 K for $M=\text{Ru}$ and Os , respectively. © 2002 Elsevier Science (USA)

INTRODUCTION

There is growing interest in oxide materials based on transition elements of the $4d$ and $5d$ series which exhibit unusual electronic properties including frustrated ($\text{Y}_2\text{Mo}_2\text{O}_7$) or low-dimensional ($\text{Sr}_3\text{CuPt}/\text{IrO}_6$) magnetism or even superconductivity ($\text{Cd}_2\text{Re}_2\text{O}_7$). (1–3) In particular, local moment magnetism is somewhat unexpected in this domain of the periodic table as binary oxides of the $4d$ and $5d$ elements are generally metallic and Pauli paramagnetic, for example MoO_2 , RuO_2 , OsO_2 and ReO_3 among others,

in contrast to the binary oxides of the more familiar $3d$ transition series which are normally magnetic. Among the most important causes of this fundamental difference are the enhanced radial extent of the $4d$ and $5d$ orbitals and the predominance of higher formal oxidation states in this part of the periodic table, both of which tend to favor broader one-electron band widths. As well, one expects the correlation energy to decrease with the increase in principal quantum number and in the context of the Mott–Hubbard model, collective electron or metallic behavior is expected.

Nonetheless, there are now a number of ternary or more complex oxides in which local moment magnetism is unequivocally associated with $4d$ or $5d$ elements. One class of materials in this category is represented by the Ln_3MO_7 series where $\text{Ln}=\text{a}$ rare earth and M is a pentavalent transition element. Examples include $M=\text{Mo}$, Ru and Ir (4–8). These compounds crystallize in a structure type which is based on an ordered double fluorite cell in which the Ln^{3+} and M^{5+} cations order along with the oxide vacancies, resulting in an orthorhombic supercell with $\mathbf{a} \approx 2\mathbf{a}_F$, $\mathbf{b} \approx \mathbf{c} \approx \sqrt{\mathbf{a}_F}$. An important feature of this structure, Fig. 1, are zig-zag chains of corner-sharing MO_6 octahedra which are well-isolated, $> 6.6 \text{ \AA}$ interchain distance, along the \mathbf{a} -axis. This quasi-one-dimensionality along with the acute $M\text{--O--}M$ intrachain angle of $\sim 145^\circ$ perhaps contribute to stabilization of the local moment ground state.

The series based on $M=\text{Ru}$ has been the most extensively studied, with results for crystal structures and physical properties for $\text{Ln}=\text{La}$, Pr , Sm and Eu (9–11). All show evidence for antiferromagnetic long-range order at temperatures ranging from ~ 17 K (La) to ~ 50 K (Pr). Surprisingly, perhaps, there is scant evidence for the expected one dimensionality in the magnetic susceptibility. In part this is due to the fact that the Ln magnetism tends to dominate when the Ln^{3+} ion is magnetic but even in

¹To whom correspondence should be addressed. Fax: 905-522-2773. E-mail: greedan@mcmaster.ca.

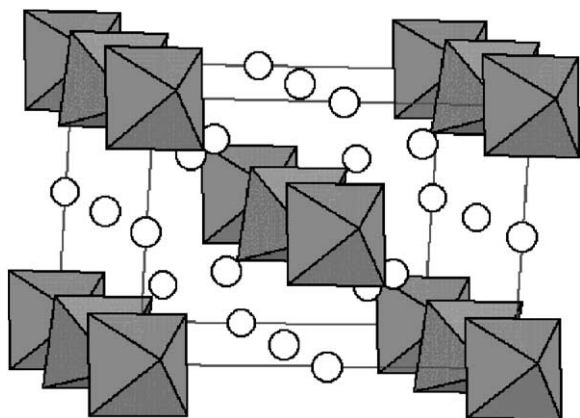


FIG. 1. A view of the crystal structure of La_3OsO_7 which emphasizes the linear chain of corner-sharing octahedra parallel to the \mathbf{a} -axis in the chosen setting. The open circles are the La^{3+} ions. Os–Os distances are 3.81 Å (intrachain) and 6.75 Å (minimum interchain).

the previous report on the La phase, features due to one-dimensional effects were not evident in the data presented (9).

The $5d$ series counterpart of Ru is of course Os. To date there have been no reported studies of Ln_3OsO_7 phases. It would be of considerable interest to compare the properties of the Os- and Ru-based materials. Clearly, the most useful comparison would be for the La member for which the effects of changing from $4d$ to $5d$ orbitals will be most transparent. To this end an attempt was made to synthesize and characterize La_3RuO_7 and La_3OsO_7 .

EXPERIMENTAL

Synthesis

La_3OsO_7 and La_3RuO_7 were isolated with greater than 95% purity from the reaction of a mixture of La_2O_3 (99.9%, Aldrich), OsO_2 (99.99%, Premion from Alfa Aesar), RuO_2 (99.9% Cerac) in a 3:2 ratio to which a stoichiometric amount of oxygen was provided by the decomposition of KClO_3 ($\geq 99\%$, Aldrich) for the Os phase and CrO_3 (98% Anachemia Ltd.) for the Ru material. Powders of the starting materials (La_2O_3 and $\text{OsO}_2/\text{RuO}_2$) were mixed in an agate mortar and pestle, pressed into a pellet, and placed in a lidded Pt container which was loaded into a quartz tube that was then evacuated ($\sim 10^{-5}$ Torr) and sealed along with a weighed amount of KClO_3 or CrO_3 (wrapped in a separate Pt foil). The firing schedules were different for the two compounds. For La_3OsO_7 the mixture was heated in a tube furnace under a constant flow of argon at 360°C for 12 h, 900°C for 1 day, cooled to 500°C over 1 day, and then cooled to room temperature over 5 h. Regular monitoring of the reaction revealed that the quartz vessel had exploded

during the cooling profile, likely caused by a reaction of the quartz with the decomposition product KCl. A white surface impurity found on the pellet was subsequently removed to reveal the desired black product inside. For La_3RuO_7 the quartz reaction tube was heated over 24 h. to 1075°C and held for 48 h and quenched to room temperature.

Caution: These reactions are prone to explosion of the quartz reaction tube due to excessive O_2 pressure if care is not taken to heat slowly and to adjust the tube volume to the amount of oxygen source used. As a precaution, the quartz tube should be enclosed in a protective outer tube of quartz or ceramic.

Magnetic Measurements

Powdered samples of ~ 100 mg were placed in a gelatin capsule holder and accurately weighed prior to data collection. Zero-field-cooled (ZFC) and field-cooled (FC) magnetic susceptibility data were collected on a Quantum Design MPMS SQUID magnetometer between 2 and 350 K with applied fields of 500 or 1000 Oe. Data between 300 and 600 K were obtained from an oven insert in an applied field of 5000 Oe. Paramagnetic susceptibilities were calculated by subtracting the diamagnetic contributions from the raw magnetic susceptibility data using Pascal's constants in emu mol^{-1} units (-1.7×10^{-4}).

X-Ray Powder Diffraction

Data were collected on a powder sample using a Bruker D8 diffractometer with $\text{CuK}\alpha$ radiation and an exit beam graphite monochromator. The resulting diffraction pattern was refined using the WINPLOTR version of FULLPROF (12).

RESULTS AND DISCUSSION

The results of a Rietveld refinement of the X-ray powder diffraction data for La_3OsO_7 in space group $Cmcm$ are collected in Tables 1 and 2. Fig. 2 shows the fit. The sample contains a very small amount of a second phase. Within the usual limitations of the analysis of powder X-ray data for oxides dominated by heavy elements, the results are reasonable. The negative displacement parameter for O(1) is an artifact of the refinement due to well-known difficulties in modeling the X-ray lineshape. The crystal structure of La_3RuO_7 has been refined recently from powder neutron diffraction data (13) and the less accurate results from powder X-ray data will not be reported here. To date there exist no neutron powder or X-ray single-crystal data for La_3OsO_7 . The unit-cell parameters (Å) for the La_3RuO_7 sample prepared here agree well with those from the literature [square brackets], $\mathbf{a} = 11.214(1)$ [11.2093(1)], $\mathbf{b} = 7.4711(7)$ [7.4617(1)] and $\mathbf{c} = 7.6071(7)$

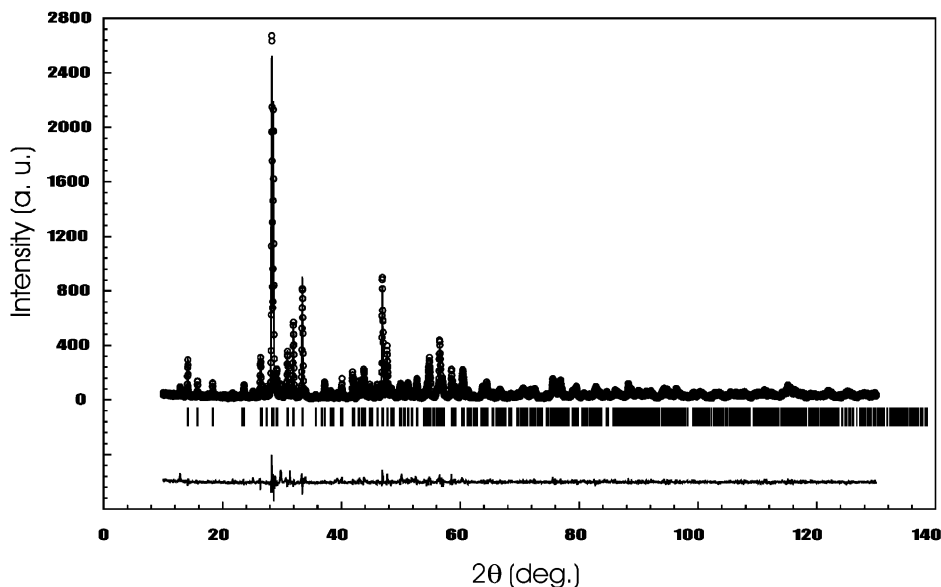


FIG. 2. Profile (Rietveld) refinement of the X-ray diffraction data of La_3OsO_7 . The open circles represent the data, the solid line is the fit, the vertical tick marks locate the Bragg peak locations and the difference plot is shown at the bottom.

value, as expected, given that this value is largely fixed by the position of $T(\chi_{\max})$, as already mentioned above.

In comparing the results for the two compounds the effect of changing from $4d$ to $5d$ orbitals is clear and significant as J^{intra}/k increases ~ 8 -fold from La_3RuO_7 to La_3OsO_7 . The enhancement of T_c , the critical temperature for long-range ordering, is less spectacular at about three-fold. It is worth noting that the ratios $|\theta_c|/T_c$ are quite different for the two materials, 0.6–0.7 for Ru and 6.2 for Os, which suggests that the magnetic structures may be different. The magnetic structure of neither material is known.

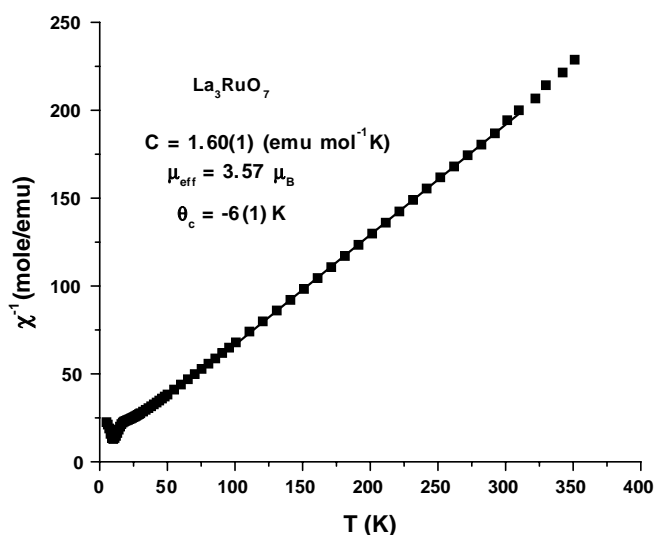


FIG. 3. Inverse susceptibility versus temperature for La_3RuO_7 showing the fit to the Curie–Weiss law.

It is important to compare these results for the Ru and Os materials with the only other case for which the M ion magnetic properties have been determined which is La_3MoO_7 (5). This compound presents a very complex behavior but the salient facts are that La_3MoO_7 is semiconducting and shows a very broad χ_{\max} at 655 K followed by what appear to be crystallographic phase transitions at lower temperatures, 483 and 373 K. Two lower temperature susceptibility anomalies also occur at

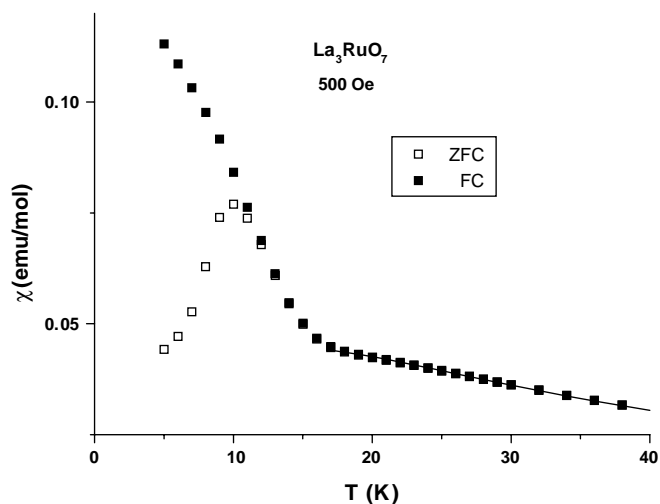


FIG. 4. The susceptibility at low temperature for La_3RuO_7 showing the sharp maximum near 10 K and the broad maximum near 20 K. Also seen is the FC-ZFC divergence associated with the sharper feature. The solid line is a fit to a model based on Weng's numerical result for the $S = \frac{3}{2}$ Heisenberg linear chain with fitting parameters $g = 1.94(5)$ and $J/k = -2.94(5)$ K (16).

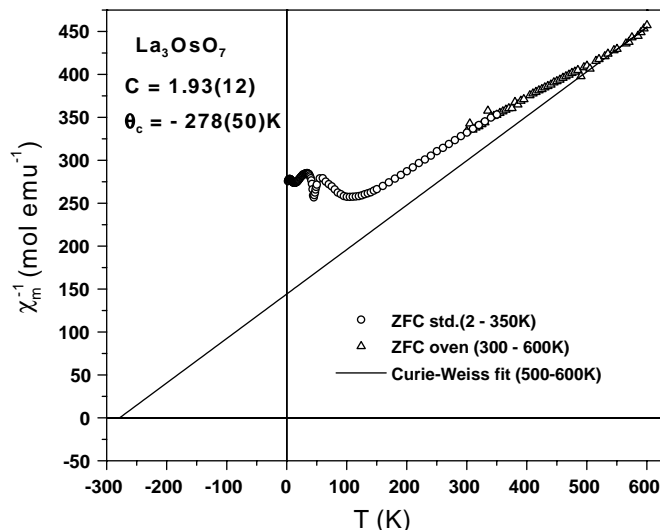


FIG. 5. Inverse susceptibility for La_3OsO_7 showing a Curie-Weiss regime only at high temperature, 500–600 K.

140 and ~ 80 K. There is some evidence that the latter is associated with long-range magnetic order from an analysis of neutron powder diffraction data but the reflections involved are very weak. No Curie-Weiss regime is seen out to 800 K. Assuming that the broad feature at 655 K is due to the same sort of one-dimensional spin correlations as for the Ru and Os phases, and recalling that for a $S = \frac{1}{2}$ ion, Mo^{5+} has a $4d^1$ configuration, $|J^{\text{intra}}/k| = T(\chi_{\text{max}})/1.282$ (15), this leads to $J^{\text{intra}} = -511$ K which is orders of magnitude larger than those seen for the $4d^3$ and $5d^3$

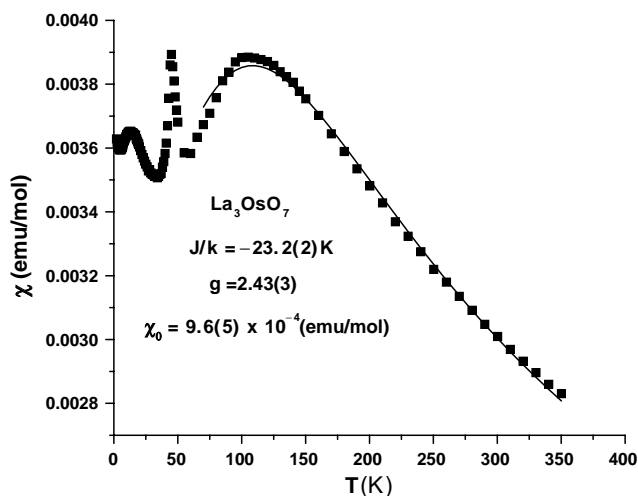


FIG. 6. Susceptibility data for La_3OsO_7 between 2 and 350 K showing a broad maximum near 110 K, a sharp maximum at 45 K and a further broad feature at ~ 15 K. The solid line is a fit to a model based on Weng's numerical result for the $S = \frac{3}{2}$ Heisenberg linear chain with fitting parameters $g = 2.43(3)$, $J/k = -23.2$ K and $\chi(\text{TIP}) = 9.6(5) \times 10^{-4}$ emu/mol (16).

configurations. These trends are not unexpected, at least semi-quantitatively, in terms of the usual Anderson formulation of superexchange in which $J \sim b^2/U^2$ (17) where b is a transfer integral which is proportional to orbital overlaps and covalency and U is the correlation energy. In general, orbital radii are more extended at the beginning of a transition series (implying larger b 's) and U increases across at least the first half of a transition series (18) which helps to explain the larger value for Mo^{5+} ($4d^1$) relative to Ru^{5+} ($4d^3$) and Os^{5+} ($5d^3$). The enhancement of J upon substituting Ru^{5+} by Os^{5+} can be traced most likely to an increase in orbital radial extent ($5d$ versus $4d$) but the role of a small decrease in U , cannot be ruled out.

CONCLUSIONS

The preparation of La_3OsO_7 has been reported for the first time. The magnetic properties of this compound were also studied and those for La_3RuO_7 were re-investigated. Both materials show evidence for nearly spin-only, $S = \frac{3}{2}$, local moment magnetism from analysis of Curie-Weiss data. The presence of one-dimensional intra-chain spin correlations are manifested in the susceptibility data in the form of broad maxima at ~ 18 K for the Ru phase and ~ 110 K for the Os material. The properties of La_3OsO_7 present the most unequivocal evidence to date for the importance of one-dimensional spin correlations which are expected due to the occurrence of spatially well-separated zig-zag chains of corner-sharing MO_6 octahedra in these compounds. Analysis in terms of a model based on Weng's numerical results for the $S = \frac{3}{2}$ Heisenberg model shows an eight-fold increase in J^{intra}/k from the Ru compound to the Os phase. This augmentation is rationalized in terms of the Anderson model for superexchange and expected increases in orbital radii and covalency and decreases in the correlation energy as one progresses down a group in the periodic table. The results for La_3MoO_7 are also compared and the very large J^{intra}/k for this $4d^1$ based material is rationalized using similar arguments. Evidence for long-range magnetic order is seen for La_3OsO_7 below 45 K but the magnetic structure is not yet known.

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