

Synthesis, Structure, and Magnetic Properties of a Novel Mixed-Valent Strontium Rhodium Oxide

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Low-dimensional materials, both one- and two-dimensional, have long been of interest to chemists and physicists because of their distinctive electronic and magnetic properties.^{1–3} Much work has been done on the halide perovskites with the BaNiO₃ structure⁴ and, recently, oxides with the K₄CdCl₆⁵ structure, such as Sr₃NiIrO₆, have been shown to exhibit interesting magnetic properties associated with their highly anisotropic structures.^{6–11} Darriet has shown that these structures are closely related¹² and, furthermore, that it should be possible to form phases with structures intermediate between those of the BaNiO₃ and K₄CdCl₆ structure types with the general formula A_{3n+3}A'_nB_{n+3}O_{9+6n} (*n* = 0, BaNiO₃; *n* = ∞, Sr₃NiIrO₆). So far, however, comparatively few oxides of this series with structures other than those of the end-members have been synthesized.^{13–22} Moreover, of these structures,

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Table 1. Summary of Rietveld Data and Least-Squares Refinement Results for Sr₆Rh₅O₁₅

space group	R32
<i>a</i> (Å)	19.3197(2)
<i>c</i> (Å)	13.0418(1)
volume (Å ³)	4215.66(9)
no. of Bragg peaks	1936
no. of refined parameters	68
no. of profile parameters	6
S	1.734
R _{exp} ^a (%)	6.32
R _{wp} ^a (%)	10.96
R _p ^a (%)	7.69
R _{Bragg} ^a (%)	2.90

^a See ref 27 for calculations of reliability factors.

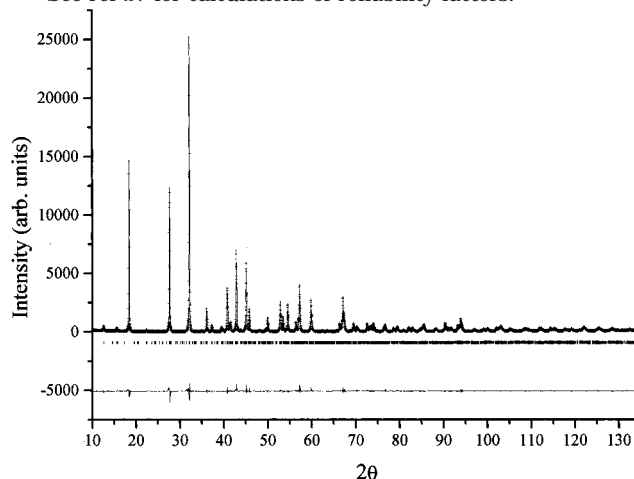


Figure 1. Observed (cross) and calculated (solid line) X-ray diffraction patterns of Sr₆Rh₅O₁₅. Tick marks indicate the positions of allowed Bragg reflections. The difference line, observed minus calculated, is located at the bottom of the figure.

the electronic properties have been reported for only one of the *n* = 1 members; Ba₆Ni₅O₁₅ is a Curie–Weiss paramagnetic insulator at all temperatures measured.¹³

In this paper we report on the synthesis, structural characterization, and preliminary analysis of the magnetic properties of Sr₆Rh₅O₁₅, an *n* = 1 member of the series A_{3n+3}A'_nB_{n+3}O_{9+6n}.

Polycrystalline Sr₆Rh₅O₁₅ was synthesized via a solid-state reaction. SrCO₃ (Alfa, 99.95%) and Rh metal (Engelhard, 99.95%) were intimately mixed and thoroughly ground, followed by pressing the powder into pellets and placing them into alumina crucibles. The pellets were initially heated in air at 850 °C for 10 h and then at 1150 °C for 9 days with intermittent grinding. The X-ray powder diffraction data were collected on a Rigaku D\Max-2200 powder X-ray diffractometer with Bragg–Brentano geometry using Cu Kα radiation. The step-scan covered the angular range 10°–135° 2θ in steps of 0.02° 2θ.

Structure refinements of Sr₆Rh₅O₁₅ were carried out in the space group R32 (No. 155) using the Rietveld method implemented in the computer programs GSAS²³ and RIETAN.^{24,25} Both programs yielded similar re-

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Table 2. Atomic Positions (and Esds) for Sr₆Rh₅O₁₅^a

atom	site	x	y	z	atom	site	x	y	z
Sr(1)	9d	-0.160(1)	0	0	O(1)	18f	-0.236(5)	-0.087(6)	0.523(7)
Sr(2)	9d	0.338(1)	0	0	O(2)	18f	0.247(6)	-0.076(5)	0.531(6)
Sr(3)	18f	0.335(1)	0.499(1)	0.0102(6)	O(3)	18f	-0.244(6)	0.416(5)	0.520(7)
Sr(4)	9e	-0.321(1)	0	0.5	O(4)	18f	0.257(7)	0.413(6)	0.525(6)
Sr(5)	9e	0.179(1)	0	0.5	O(5)	9d	0.078(6)	0	0
Sr(6)	18f	0.178(1)	0.504(1)	0.499(1)	O(6)	9d	-0.415(9)	0	0
Rh(1)	6c	0	0	0.095(2)	O(7)	18f	0.414(6)	-0.087(5)	0.002(9)
Rh(2)	18f	0.500(1)	0.000(1)	0.0960(6)	O(8)	18f	-0.158(6)	-0.259(4)	0.066(6)
Rh(3)	6c	0	0	0.291(2)	O(9)	18f	0.315(4)	-0.259(4)	0.048(5)
Rh(4)	18f	0.499(1)	-0.002(1)	0.2911(6)	O(10)	18f	-0.151(5)	0.250(5)	0.053(6)
Rh(5)	3b	0	0	0.5	O(11)	18f	0.360(4)	0.252(5)	0.059(5)
Rh(6)	9e	0.500(1)	0	0.5					

^a An overall thermal parameter Q (0.16(2) Å²) was used in the refinement. Q is defined as an isotropic thermal (B) applied to each individual atom in the structure.

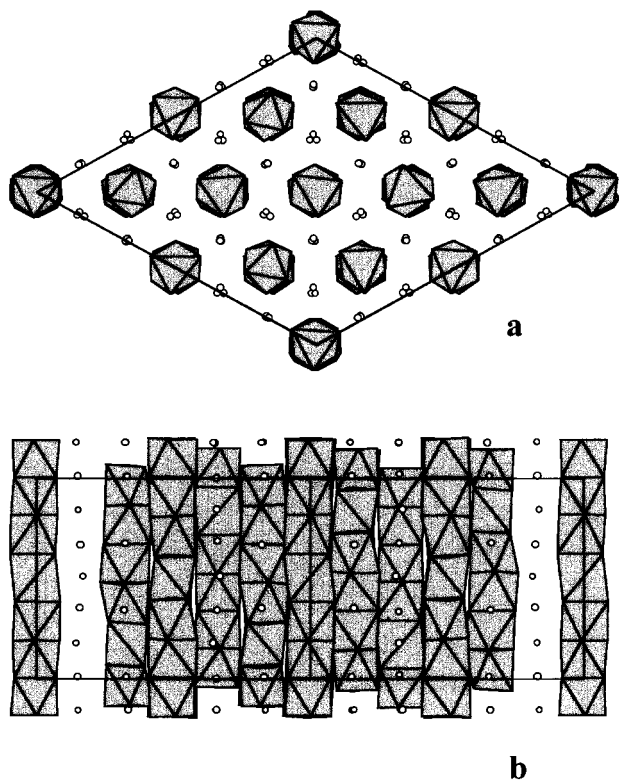


Figure 2. Structure of Sr₆Rh₅O₁₅ (a) viewed along the c -axis and (b) along [110]. Sr cations are white circles; RhO₆ polyhedra are shaded gray.

sults, and only those using RIETAN will be discussed. $R\bar{3}$ (No. 146), $R\bar{3}$ (No. 148), $R3m$ (No. 160), and $R\bar{3}m$ (No. 166) are also consistent with the observed extinctions. Therefore, refinements were also carried out in $R\bar{3}$, $R\bar{3}$, and $R3m$. Both $R\bar{3}$ and $R3m$ gave significantly worse refinements than $R\bar{3}2$ ($R\bar{3}m$ is a supergroup of $R\bar{3}$ and $R3m$ and was thus not refined). $R\bar{3}$ gave a marginally better refinement, (R_{wp} 10.81 vs R_{wp} 10.96); however, the number of parameters was greatly increased and the atoms remained very close to the positions for $R\bar{3}2$, making it a less satisfactory solution. Consequently, we report the structure in $R\bar{3}2$. Estimated standard deviations were calculated using the

method of Scott,²⁶ which yields larger values than the conventional method, though more physically realistic. The profile of the diffraction peaks of Sr₆Rh₅O₁₅ was described by a pseudo-Voigt function. An overall thermal parameter and March–Dollase preferred orientation parameter were refined. Refinement of the peak asymmetry was allowed, and the background was described by a polynomial function with eight refineable coefficients.

Details of the Rietveld refinement of Sr₆Rh₅O₁₅ are given in Table 1. The best agreement obtained between the calculated and the observed profiles for Sr₆Rh₅O₁₅ is shown in Figure 1. The atomic positions for Sr₆Rh₅O₁₅ can be found in Table 2. Sr₆Rh₅O₁₅ is closely related to the known compounds Sr₆Co₅O₁₅¹⁴ and Ba₆Ni₅O₁₅,¹³ however, to account for all the observed diffraction peaks, the unit cell was transformed ($a' = -2a$, $b' = -2b$). Attempts to index the extra peaks on the basis of the incommensurately modulated composite structure observed for several related oxides^{15,28} were unsuccessful. The rhombohedral structure consists of two types of crystallographically distinct infinite one-dimensional chains of tetramers composed of face-sharing RhO₆ octahedra linked by RhO₆ trigonal prisms; these infinite chains themselves are separated by chains of Sr cations. The structure is shown in Figure 2. The differences between the Sr₆Rh₅O₁₅ structure and the Sr₆Co₅O₁₅ structure appear to be due to a distortion of the strontium chains. Comparisons of the heavy atom positions between the average structure solved in the Sr₆Co₅O₁₅ cell and the larger cell give only small shifts (<0.07 Å) for all the atoms except Sr(3), which shifts 0.36(4) Å toward the trigonal prisms centered by Rh(5). This is presumably caused by alternations in Rh–O bond distances due to charge ordering. However, given the limitations of the current data set, collected on a laboratory X-ray powder diffractometer, there exist

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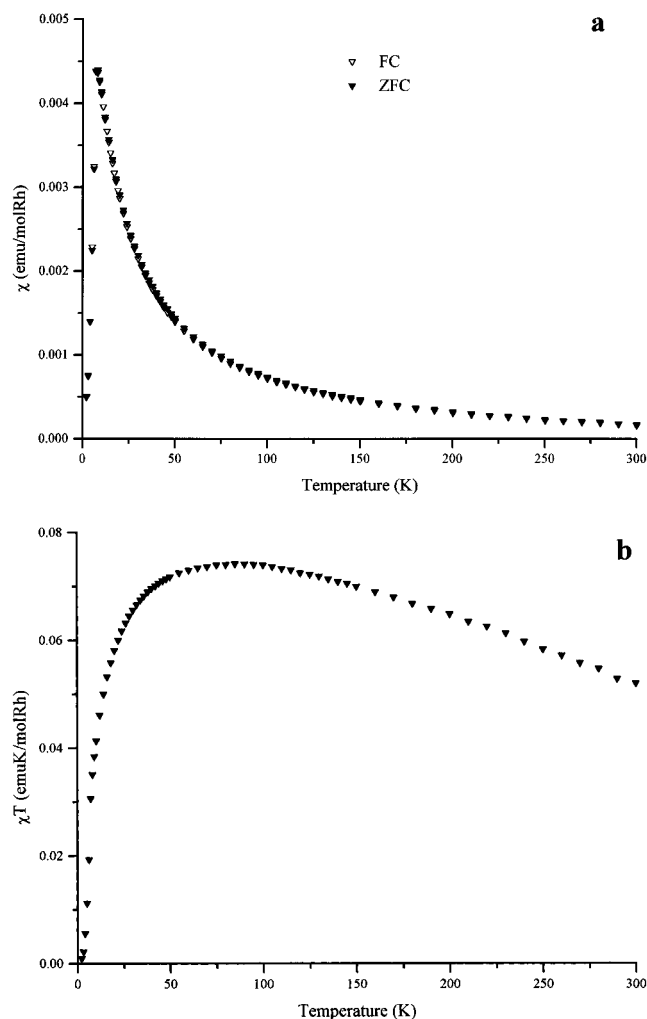


Figure 3. (a) Temperature dependence of the magnetic susceptibility measured at 5 kG and (b) a χT plot measured at 5 kG for $\text{Sr}_6\text{Rh}_5\text{O}_{15}$.

sufficiently large uncertainties in the oxygen positions as to preclude assignment of the oxidation states of the rhodium atoms based upon their metal oxygen bond lengths. Further studies using synchrotron XRD and/or neutron diffraction in order to locate the oxygen atoms precisely would undoubtedly provide more structural information.

The magnetic susceptibility of $\text{Sr}_6\text{Rh}_5\text{O}_{15}$ was measured using a Quantum Design MPMS XL SQUID magnetometer. The temperature dependencies of the susceptibilities were measured under both field-cooled (FC) and zero-field-cooled (ZFC) conditions by heating the samples from 2 to 300 K in applied fields of 5 and 40 kG. The small diamagnetic contribution of the sample holder was corrected for by subtraction of a blank run. Figure 3a shows the magnetic susceptibility for $\text{Sr}_6\text{Rh}_5\text{O}_{15}$ measured at 5 kG both FC and ZFC, and Figure 3b shows a plot of χT versus T for the ZFC data collected in the 5 kG field. Between 300 and 150 K,

the system follows the Curie–Weiss law. The measured Curie–Weiss parameters, $C = 0.055(1)$ emu K/mol (Rh), $\theta = 28(2)$ K, and $\mu_{\text{eff}} = 0.66(3)\mu_{\text{B}}$, correspond to one unpaired electron per cluster (tetramer of octahedra plus trigonal prismatic site) containing five rhodium cations (spin only value of $0.66\mu_{\text{B}}$). One assignment of Rh^{III} and Rh^{IV} to trigonal prismatic and octahedral sites in the chains that is consistent with the magnetic data is as follows: Rh^{III} occupies all the trigonal prismatic sites and one of the octahedral sites, while Rh^{IV} occupies the remaining three octahedral sites. An average of only one unpaired electron per tetramer can arise due to metal–metal interactions, either Rh–O–Rh or direct Rh–Rh interactions within the tetramer, consistent with the very short Rh–Rh distances (particularly Rh1–Rh1 and Rh2–Rh2). Similar metal–metal interactions have been suggested for the structurally closely related BaNiO_3 .^{29,30} These tetramers are weakly ferromagnetically coupled *intra*chain; the existence of this ferromagnetic coupling is supported by the positive Weiss constant and the increase in the magnetic moment (χT) with decreasing temperature, as seen in Figure 3b. There is an antiferromagnetic transition at 7 K followed by a precipitous drop in susceptibility below 7 K. The drop in susceptibility is greater than that predicted by most magnetic models for a randomly oriented powder, where the susceptibility is expected to drop to $2/3$ of χ_{max} . Similar drops in the susceptibility have been observed for several related chain type oxides such as $\text{Ca}_3\text{Co}_2\text{O}_6$ ¹¹ and $\text{Sr}_3\text{NiIrO}_6$.^{8,31} and in cluster systems. However, in the chain type oxides the systems are magnetically frustrated, whereas in the cluster systems the transitions are broad. For $\text{Sr}_6\text{Rh}_5\text{O}_{15}$, the transition is relatively sharp and the FC and ZFC measurements are virtually identical, indicating that the spins are not magnetically frustrated below 7 K. Conductivity measurements, carried out on a pressed pellet between 300 and 15 K, support the conclusion that the material is a semiconductor/insulator.

In conclusion, we have synthesized $\text{Sr}_6\text{Rh}_5\text{O}_{15}$ which crystallizes in a novel superstructure of the $\text{Sr}_6\text{Co}_5\text{O}_{15}$ type. The compound is a paramagnetic semiconductor above 7 K, below which temperature an antiferromagnetic transition occurs.

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Supporting Information Available: Listings of bond distances, Rietan list file, and calculated and observed peak positions (11 pages). Ordering information is given on any current masthead page.

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