

Magnetic properties of $\text{BaRu}_{1-x}\text{Rh}_x\text{O}_3$ and $\text{Sr}_2\text{Ru}_{1-x}\text{Rh}_x\text{O}_4$

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The magnetic susceptibilities of polycrystalline $\text{BaRu}_{1-x}\text{Rh}_x\text{O}_3$ ($x = \frac{1}{3}, \frac{1}{2}$) and $\text{Sr}_2\text{Ru}_{1-x}\text{Rh}_x\text{O}_4$ ($x = \frac{1}{2}, \frac{2}{3}$) have been measured as a function of temperature. In all cases hysteresis is apparent below ~ 100 K, and the zero-field-cooled susceptibility of $\text{Sr}_2\text{Ru}_{1-x}\text{Rh}_x\text{O}_4$ shows a maximum below 20 K. The data suggest an increase in the extent of electron localization in comparison with isostructural compounds (BaRuO_3 , Sr_2RuO_4 , and Sr_2RhO_4), but there is no evidence for the weak ferromagnetism found in the Ir analogs (BaIrO_3 and Sr_2IrO_4).

INTRODUCTION

The discovery of superconductivity at relatively high temperatures in mixed-valence oxides of copper prompted a great deal of research into the solid state chemistry of that element. With the passage of time, the scope of this activity has broadened to include oxides of transition metals other than copper, with particular emphasis being placed on perovskite-related compounds containing elements from the second and third transition series. These metals occur in relatively high oxidation states ($\geq +3$), usually with ≤ 6 d electrons per cation, and, in the strength of crystal field found in an oxide environment, they usually adopt a low-spin configuration. In this case the $e_g(\sigma^*)$ band, which is partially filled in $\text{Cu}^{2+}/\text{Cu}^{3+}$ compounds, is empty and the electronic properties of the material are determined by the electron concentration in the lower energy $t_{2g}(\pi)$ band. Although these two energy levels have different symmetries, there is a hope that a partially filled t_{2g} band might give rise to the same remarkable properties that have been found in the perovskite-related Cu compounds. The work carried out to date has not led to the discovery of new "high T_c " superconductors, but it has revealed that these compounds can show a wide variety of electronic properties. Crawford *et al.*¹ have shown that Sr_2IrO_4 (isostructural with K_2NiF_4) is weakly ferromagnetic below ~ 250 K, whereas the isoelectronic ($5d$ electrons per transition metal cation) compound Sr_2RhO_4 is metallic and shows no spontaneous magnetization.^{2,3} The properties of Sr_2RuO_4 (d^4) are similar to those of the Rh analog. Similarly, although the rhombohedral perovskite $9R\text{-BaRuO}_3$ (d^4) is a paramagnetic metal,^{4,5} the essentially isostructural material BaIrO_3 (d^5) is a weak ferromagnet.⁶

Recently there has been a particular emphasis on both layered³ and three-dimensional⁷ Rh-containing materials, the aim being to control the average oxidation state of the cation, and hence the electron concentration in the t_{2g} band, by means of chemical substitution. This research program has involved the synthesis of $\text{La}_{1-x}\text{M}_x\text{RhO}_3$ ($M = \text{Ca}, \text{Sr}, \text{Ba}$) (Ref. 7) and $\text{Sr}_{2-x}\text{La}_x\text{RhO}_4$,³ both of which can be thought of as mixed valence Rh(III)/Rh(IV) compounds. The members of the latter series are metallic for $x \leq 0.15$ and

semiconducting for $x \geq 0.20$, whereas the members of the former series are all paramagnetic semiconductors. We too have initiated a study of Rh oxides, but rather than varying the occupation of the t_{2g} band by making substitutions among the diamagnetic cations, we have chosen to introduce a second transition metal species. Thus we have studied the magnetic properties of $\text{BaRu}_{2/3}\text{Rh}_{1/3}\text{O}_3$ and $\text{BaRu}_{1/2}\text{Rh}_{1/2}\text{O}_3$, having an average of 4.33 and 4.50

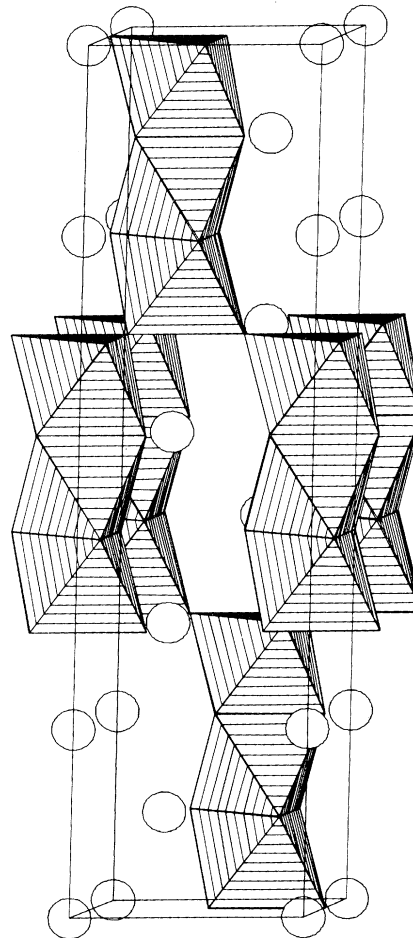


FIG. 1. The crystal structure of BaRuO_3 .

d electrons per transition metal cation, respectively. It has been shown previously⁸ that these compounds are isostructural with 9R-BaRuO₃, the somewhat anisotropic structure of which is drawn in Fig. 1. We have adopted a similar strategy in our study of the K₂NiF₄ phases Sr₂Ru_{1/3}Rh_{2/3}O₄ and Sr₂Ru_{1/2}Ru_{1/2}O₄ ($d^{4.66}$ and $d^{4.5}$, respectively). The results of this work are described below.

EXPERIMENT

Polycrystalline samples of composition BaRu_{1-x}Rh_xO₃ were prepared in alumina crucibles by firing the appropriate stoichiometric quantities of RuO₂, Rh₂O₃ and BaCO₃ (Johnson Matthey Chemicals) in air at temperatures of up to 1200 °C for several days. Samples of Sr₂Ru_{1-x}Rh_xO₄ were prepared by firing intimately ground mixtures of SrCO₃, RuO₂, and Rh₂O₃ at 1200 °C in a flow of oxygen gas. The progress of the reactions was monitored by x-ray powder diffraction using a Philips PW1710 diffractometer, operating with Cu $K\alpha$ radiation in Bragg-Brentano geometry, at a 2θ step size of 0.02°. The magnetic susceptibilities of the monophasic products were measured in a magnetic field of 5 kG over the temperature range $6 \leq T \leq 296$ K using a CCL SCU500 superconducting quantum interference device magnetometer; data were collected after cooling the sample from room temperature in zero applied field (ZFC) and after cooling in the measuring field (FC).

RESULTS

Single phase samples of BaRu_{1-x}Rh_xO₃ were obtained for $x = \frac{1}{3}$ and $\frac{1}{2}$. The x-ray diffraction data confirmed that these two compositions are isostructural with rhombohedral BaRuO₃, as proposed previously.⁸ The unit cell parameters refined to the values $a = 5.7466(4)$, $c = 21.726(2)$ Å for $x = \frac{1}{3}$ and $a = 5.7534(4)$, $c = 21.762(2)$ for $x = \frac{1}{2}$. Structure refinements performed in space group $R\bar{3}m$ using the GSAS program suite⁹ showed good agreement between the observed and calculated intensity distribution for both samples [$R_I = 5.1\%$ ($x = \frac{1}{3}$), $R_I = 4.24\%$ ($x = \frac{1}{2}$)], with no evidence for vacancies on the anion sublattice in either case. However, we do not wish to overinterpret the results of this attempt to locate the weakly scattering oxide ions. Samples having $x \geq \frac{2}{3}$ were not monophasic and will not be discussed further here. Single phase K₂NiF₄-like samples of Sr₂Ru_{1-x}Rh_xO₄ were obtained for $x = \frac{1}{2}$ and $x = \frac{2}{3}$. The x-ray data were analyzed assuming tetragonal symmetry, as found for Sr₂RuO₄,¹⁰ and also in orthorhombic symmetry, as found for Sr₂RhO₄.² There was no significant improvement in the agreement between the observed and calculated diffraction patterns on lowering the symmetry, and we shall therefore present the results of the analysis carried out in space group $I4/mmm$. The unit cell parameters refined to the values $a = 3.8775(2)$, $c = 12.7818(5)$ Å for $x = \frac{1}{2}$ and $a = 3.8714(2)$, $c = 12.8118(7)$ Å for $x = \frac{2}{3}$. Again, there was good agreement between the observed and calculated intensity distributions [$R_I = 2.2\%$ ($x = \frac{1}{2}$), $R_I = 2.7\%$ ($x = \frac{2}{3}$)]. The

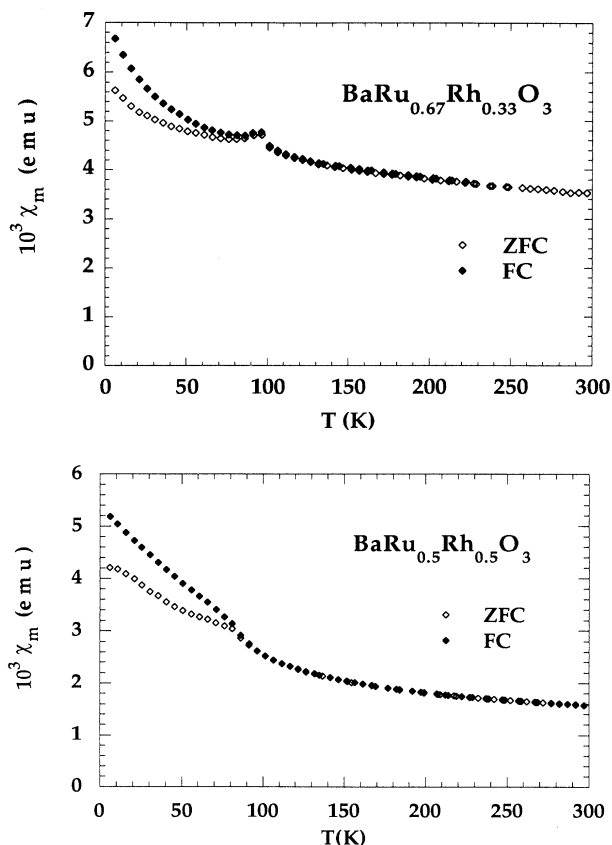


FIG. 2. The temperature dependence of the molar magnetic susceptibilities of BaRu_{1-x}Rh_xO₃ for $x = \frac{1}{3}, \frac{1}{2}$.

molar magnetic susceptibilities of the compounds BaRu_{1-x}Rh_xO₃ are plotted in Fig. 2. Both compositions show only a weak temperature dependence, particularly above 100 K. The data collected under ZFC and FC conditions agree well at high temperatures, but hysteresis is apparent below 97 K ($x = \frac{1}{3}$) or 87 K ($x = \frac{1}{2}$). The susceptibility of BaRu_{0.67}Rh_{0.33}O₃ shows a clear local maximum at 97 K. Attempts to fit the high temperature ($T > 150$ K) data to a Curie-Weiss law resulted in the values $\theta = -920$ K, $\mu_{\text{eff}} = 5.8\mu_B$ ($x = \frac{1}{3}$) and

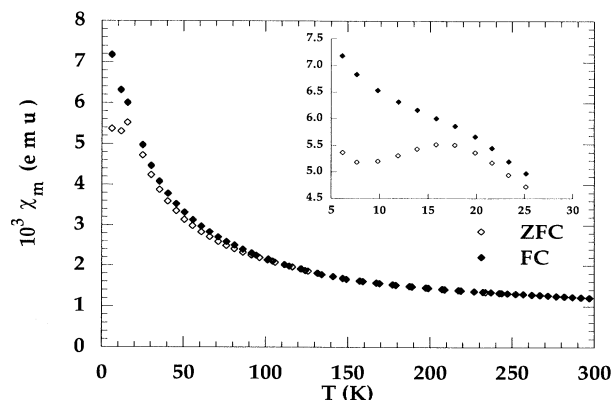


FIG. 3. The temperature dependence of the molar magnetic susceptibility of Sr₂Ru_{0.5}Rh_{0.5}O₄.

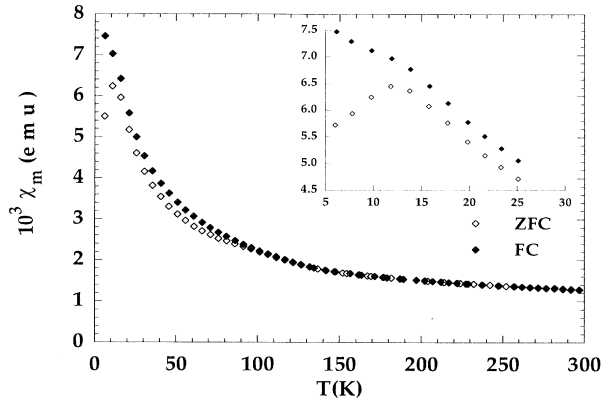


FIG. 4. The temperature dependence of the molar magnetic susceptibility of $\text{Sr}_2\text{Ru}_{0.33}\text{Rh}_{0.67}\text{O}_4$.

$\theta = -375$ K, $\mu_{\text{eff}} = 2.9\mu_B$ ($x = \frac{1}{2}$). The data collected on $\text{Sr}_2\text{Ru}_{1-x}\text{Rh}_x\text{O}_4$ are plotted in Fig. 3 ($x = \frac{1}{2}$) and Fig. 4 ($x = \frac{2}{3}$). Both compositions exhibit hysteresis below ~ 100 K, and the ZFC (but not the FC) susceptibilities have maxima at 17 and 13 K, respectively. The high temperature Curie-Weiss parameters are $\theta = -323$ K, $\mu_{\text{eff}} = 2.51\mu_B$ for $x = \frac{2}{3}$ and $\theta = -259$ K, $\mu_{\text{eff}} = 2.3\mu_B$ for $x = \frac{1}{2}$.

DISCUSSION

The magnetic properties of $\text{BaRu}_{1-x}\text{Rh}_x\text{O}_3$ can be contrasted with those of metallic BaRuO_3 which has 4 d electrons per transition metal cation. The magnetic susceptibility of the latter compound is only slightly temperature dependent,¹¹ and $\sim 0.5 \times 10^{-3}$ emu can be taken as a representative value in the temperature range under discussion. No hysteresis is apparent for $6 \leq T \leq 296$ K.¹² The susceptibility of the Rh-doped samples is thus an order of magnitude greater than that of BaRuO_3 , and is comparable to the values reported¹³ for insulating oxides of Ir(IV), a low spin d^5 species having $S = \frac{1}{2}$. Recent photoelectron spectroscopy measurements⁵ have shown that the magnetic susceptibility of BaRuO_3 is itself enhanced by a factor of 12 over the independent-electron value calculated from the density of states at the Fermi energy. These results suggest that the disorder created on the transition metal sublattice when some of the Ru is replaced by Rh leaves the system a significant distance away from the itinerant extreme of electron behavior. The relatively slight hysteresis observed at low temperatures shows that there are significant interactions between the magnetic moments localized on different cations, and that these interactions are frustrated in some way. It is likely that short range, but not long range, magnetic order is present in these compounds at low temperatures, a hypothesis that could be confirmed by a neutron scattering experiment. The enhancement of the susceptibility and the presence of this magnetic coupling indicate that the data cannot sensibly be interpreted in terms of band theory and Pauli paramagnetism alone. However, the Weiss temperatures, θ , reported above are considerably greater than those expected for a truly local-

ized electron system which shows no magnetic phase transition above 100 K; this is particularly true for the sample with the lower concentration of Rh dopant. The values of the effective magnetic moment, μ_{eff} , are also higher than predicted, whatever combination of cation oxidation states [that is Rh(IV) and Ru(IV), or Rh(III) and a mixture of Ru(IV)/Ru(V)] is assumed in the calculation of the expected value. A similar enhancement of these parameters has been observed previously¹⁴ in Ru oxides in which the 4*d* band is known to have a significant width although the compounds remain nonmetallic. It was suggested that these materials lie close to the border between the localized and itinerant electron regimes, and it is likely that the same is true of the materials presently under discussion. It is difficult to identify the cause of the magnetic frustration on the basis of our susceptibility data alone, but similar effects have been observed in other compounds containing either a low concentration of localized magnetic moments or two different cation species which give rise to competing superexchange interactions of comparable strengths.¹⁵ The behavior of $\text{BaRu}_{1-x}\text{Rh}_x\text{O}_3$ can also be contrasted with that of the isostructural compound $\text{BaIrO}_{3-\delta}$ (Ref. 6) (d^5 for $\delta = 0$) which is ferromagnetic below 170 K. The cation disorder apparently quenches both the independent-electron behavior found in BaRuO_3 and the spontaneous magnetism of $\text{BaIrO}_{3-\delta}$. Similar effects are seen in the $\text{Sr}_2\text{Ru}_{1-x}\text{Rh}_x\text{O}_4$ series. The magnetic susceptibilities of our samples are large enough to suggest that localized moments are present, and they show a much stronger temperature dependence than was observed for either of the metallic compounds Sr_2RhO_4 (Ref. 2) and Sr_2RuO_4 ,^{4,16} but there is no evidence of the weak ferromagnetism observed in the insulator Sr_2IrO_4 .¹ The values of θ and μ_{eff} are closer to the values expected for a localized electron system in the case of the K_2NiF_4 -like compounds than they were in the case of the rhombohedral perovskites. The behavior of the former below 100 K is again indicative of frustrated interactions between localized magnetic moments. Hysteresis at temperatures significantly above a susceptibility maximum has been observed previously in disordered Cu/Ru systems, and accounted for in terms of spin-cluster formation.¹⁷ As in the case of the $\text{BaRu}_{1-x}\text{Rh}_x\text{O}_3$ system, we conclude that the disorder among the transition metal cations is influential in determining the properties of these materials. We had hoped to replace Ru by Rh in BaRuO_3 and Sr_2RuO_4 as a means of varying the total electron count in the d band, whilst maintaining the same crystal structure and retaining a metallic conductivity. However, we conclude that the energies of the 4*d* levels associated with the Rh and Ru species are sufficiently different for electron localization to occur, and we are therefore unable to use this strategy to vary, in a useful way, the d -electron concentration in the conduction band of the parent compounds.

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