Contribution from the Chemistry Department,
The University of Connecticut, Storrs, Connecticut

Magnetic Interactions in Ternary Ruthenium Oxides

By ALAN CALLAGHAN, CARL W. MOELLER, and ROLAND WARD

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The magnetic susceptibilities of six ternary ruthenium oxides in which the ruthenium atoms are in octahedral coordination with oxygen have been measured from 77 to 1000°K. The perovskite-type $SrRuO_3$ (I) is ferromagnetic ($T_C = 160 \pm 10$°K, $\theta = 161$°K, $\mu_{sat} = 0.85$ BM, high-temperature $\mu_{eff} = 2.6$ BM). The isotypic $CaRuO_3$ (II), on the other hand, may be antiferromagnetic. The Weiss temperature is negative but the Néel point, if one exists, lies below the temperature range covered ($\mu_{eff} = 3.0$ BM, $\theta = -119$°). Sr_2RuO_4 (III) (K_2NiF_4 structure) shows an almost constant paramagnetism over a temperature range of 700°. $BaRuO_3$ (IV), $(Ba_{5/6}Sr_{1/6})RuO_3$ (V), and $Ba(Ru_{2/3}Mg_{1/3})O_3$ (VI) all contain RuO_6 octahedra sharing faces. The first has strings of three octahedra sharing two faces connected by corner sharing of the outermost octahedra to adjacent strings; the second has two face-sharing octahedra connected to other pairs by corner sharing, while the third has two face-sharing octahedra connected by corner sharing through a MgO_6 octahedron. The latter contains Ru(V). These three compounds all exhibit a low paramagnetism. The χ_m–T plots for IV and VI show broad maxima at 430 and 390°K, respectively, whereas for V there is no maximum and only a slight temperature dependence. All of the substances are good conductors except VI. The magnetic behavior of IV, V, and VI is interpreted as evidence for metal–metal bonds between the ruthenium atoms in face-shared octahedra, and the data for VI agree well with Kambe's model for a spin-coupled binuclear system. $SrRuO_3$ appears to offer the first example of ferromagnetism attributable solely to a period 5 transition metal.

Introduction

A simple relationship among the structures of a large number of ternary oxides containing large cations (A) can be found on the basis of the close-packing of AO_3 layers.[1] Cubic or hexagonal stacking or alternations of these layers result in O_6 octahedra sharing corners or faces, respectively. The smaller cations, which occupy all of these octahedra in compounds of the type AMO_3, are thus brought together either by sharing one oxygen (corner sharing) or by sharing three oxygens (face sharing). The Madelung energies of compounds with different structures of these types cannot be very different, and it has been proposed[1,2] that the hexagonal close-packing sequences result from the formation of an M–M bond sufficiently strong to overcome the increase in coulombic repulsion.

A series of ternary oxides of ruthenium provides an interesting sequence of structures in which RuO_6 octahedra are to be found in various juxtapositions.[3,4] In $BaRuO_3$ a nine-layer structure in which the sequence is hhc contains, along the *c* axis, strings of three face-sharing RuO_6 octahedra connected by corner sharing of the end octahedra (Figure 1(i)). Partial substitution of the barium with strontium gives, at composition $(Ba_{5/6}Sr_{1/6})RuO_3$, a four-layer structure with stacking sequence hc containing pairs of RuO_6 octahedra connected by corner sharing (Figure 1(ii)). In $SrRuO_3$ and $CaRuO_3$ (perovskite structure) the RuO_6 octahedra share only corners, each oxygen being common to two rutheniums (Figure 1(iii)). $Ba(Ru_{2/3}Mg_{1/3})O_3$ has the ordered hexagonal barium titanate (hcc) structure in which pairs of face-sharing RuO_6 octahedra are connected through corner sharing with MgO_6 octahedra (Figure 1(iv)). The ruthenium in this compound is mostly pentavalent. Finally, we have Sr_2RuO_4,[5] which does not conform to the close-packed layer type but has the K_2NiF_4 structure in which the RuO_6 octahedra lie in infinite layers sharing four equatorial oxygens.

This paper describes the determination of the magnetic properties of all of these compounds. The results lend support to the concept of metal–metal bonds in the compounds with hexagonal stacking sequences.

Experimental Section

Magnetic Measurements.—Magnetic susceptibilities were measured on an enclosed Gouy balance from 77 to 1000°K. Low temperatures were obtained utilizing the slow warming of a mass of copper powder cooled in liquid nitrogen, and high temperatures, by a small tubular furnace, noninductively wound. A low-temperature calibration was performed using $CuSO_4 \cdot 5H_2O$ ($\chi_g = 5.92 \times 10^{-6}$ cgs unit at 20°), and a plot of $1/\chi_m$ *vs.* T gave a straight line whose slope and intercept were in agreement with literature values. At low temperatures a pressure of 50 cm of dry helium was maintained in the balance case, and at high temperatures, 10 cm was maintained. The susceptibility of each sample was measured at three field strengths at both room temperature and 77°K to test for ferromagnetic impurities, and the molar susceptibility of each sample was corrected for the underlying diamagnetism.[6] For $SrRuO_3$, Sr_2RuO_4, and $(Ba_{5/6}Sr_{1/6})RuO_3$, several runs were performed on two or more samples. For the other compounds two or more runs were performed on a single sample. The weight changes in the magnetic field were always in excess of 4 mg and could be measured to ±0.02 mg, so the precision within a given run is considered to be better than ±1%. Because of the errors inherent in packing and calibration, the errors in the over-all susceptibility values are likely to be about ±5%.

Preparation of Materials.—The preparation of these materials has already been described by Randall[5] ($CaRuO_3$, $SrRuO_3$, Sr_2RuO_4) and Donohue[3,4] ($(Ba_{5/6}Sr_{1/6})RuO_3$, $Ba(Ru_{2/3}Mg_{1/3})O_3$, and $BaRuO_3$). They are all easily prepared by calcining appropriate mixtures of the alkaline earth carbonates or peroxides

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[1] L. Katz and R. Ward, *Inorg. Chem.*, **3**, 205 (1964).

[2] J. G. Dickinson, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **83**, 3026 (1961).

[3] P. C. Donohue, L. Katz, and R. Ward, *Inorg. Chem.*, **4**, 306 (1965).

[4] P. C. Donohue, L. Katz, and R. Ward, *ibid.*, **5**, 335 (1966).

[5] J. J. Randall and R. Ward, *J. Am. Chem. Soc.*, **81**, 2629 (1959).

[6] P. W. Selwood, "Magnetochemistry," Interscience Publishers, Inc., New York, N. Y., 1956, p 78.

TABLE I

MAGNETIC, STRUCTURAL, AND CONDUCTIVITY PROPERTIES OF SOME TERNARY RUTHENIUM OXIDES

	$CaRuO_3$	$SrRuO_3$	$BaRuO_3$	$(Ba_{5/6}Sr_{1/6})RuO_3$	$Ba(Ru_{2/3}Mg_{1/3})O_3$	Sr_2RuO_4
Structure	Perovskite	Perovskite	Nine layer	Four layer (high-temp $BaMnO_3$)	Ordered hex $BaTiO_3$	K_2NiF_4
Magnetic order	Possibly antiferro	Ferro	Antiferro	Antiferro	Antiferro	Temp-indep susceptibility
T_N or T_C, °K	<77	160	430		390	
High-temp μ_{eff}, BM	3.0	2.6				
Saturation moment		0.85				
θ, °K	−119	+161				
Conductivity	Good	Metallic, $\sim 10^{-3}$ ohm-cm	Good	Good	Poor	Medium

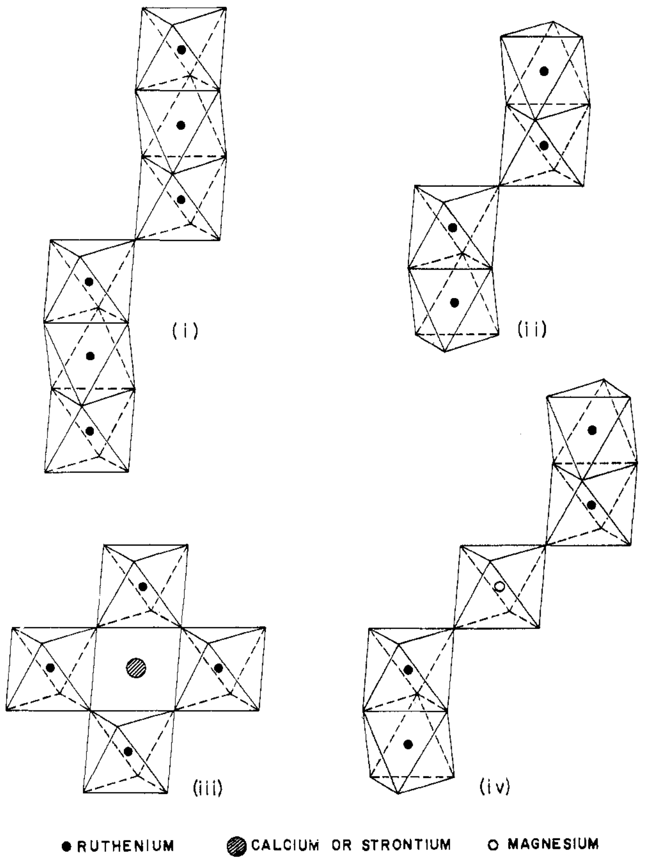

Figure 1.—Structures of some ternary ruthenium oxides: (i) $BaRuO_3$; (ii) $(Ba_{5/6}Sr_{1/6})RuO_3$; (iii) $CaRuO_3$ and $SrRuO_3$; (iv) $Ba(Ru_{2/3}Mg_{1/3})O_3$.

with ruthenium metal (200 mesh) in air at temperatures between 1000 and 1200°.

$CaRuO_3$.—Figure 2 gives the $1/\chi_m$ *vs.* T plot for $CaRuO_3$, and Tables I and II give the magnetic data. The compound has a negative Weiss temperature and follows a Curie–Weiss law at high temperatures. There is no minimum in $1/\chi_m$ down to 77°K, and so, if the compound is antiferromagnetic, the Néel point must be below this. The deviation from the straight line at low temperatures could be due to some short-range order above T_N. A compressed pellet of the material was a good conductor at room temperature.

$SrRuO_3$.—$SrRuO_3$ becomes ferromagnetic at low temperatures, and this may be the first example of ferromagnetism attributable solely to a period 5 transition metal. The position of the Curie point (T_C) was estimated by noting the temperature range within which the sample had the greatest decrease in magnetization. This placed T_C at 160 ± 10°K. The plot of $1/\chi_m$ *vs.* T above T_C is compared with that of $CaRuO_3$ in Figure 2 and shows that a Curie–Weiss law is followed, except at the lower temperatures where the deviation again may be due to persistence of short-range order. The data are summarized in Tables I and III.

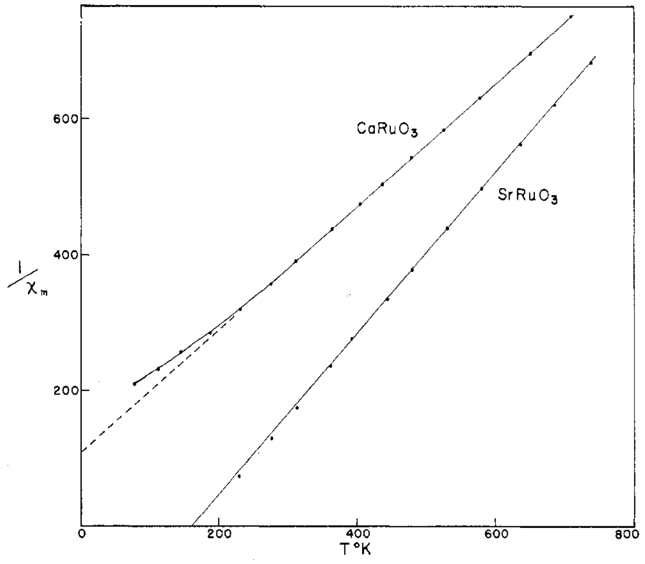

Figure 2.—Inverse molar susceptibility *vs.* temperature for $CaRuO_3$ and $SrRuO_3$.

TABLE II

MAGNETIC SUSCEPTIBILITY OF $CaRuO_3$

$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K
4.76	77	2.79	276	1.84	479
4.34	112	2.55	312	1.71	525
3.93	145	2.28	365	1.58	578
3.50	188	2.11	405	1.43	651
3.14	230	1.99	437	1.33	710

TABLE III

MAGNETIC SUSCEPTIBILITY OF $SrRuO_3$

$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K
33.7	187	5.70	313	2.28	531
24.8	196	4.22	361	2.01	579
17.5	212	3.61	393	1.77	636
13.6	228	2.97	446	1.61	686
7.74	276	2.64	481	1.46	738

Measurements of the conductivity and magnetization of $SrRuO_3$ were performed over a range of temperature and field strengths. The material proved to be a metallic-type conductor with a resistivity of 7.4×10^{-4} ohm-cm at 4.7°K and 2.4×10^{-3} ohm-cm at 300°K. There was no indication of an anomaly at T_C. These values were obtained from a powder compaction and are likely to be considerably higher than would be those from a single crystal. The magnetization of the specimen was measured at 77°K using a series of field strengths up to 10,000 oersteds. The saturation magnetization was esti-

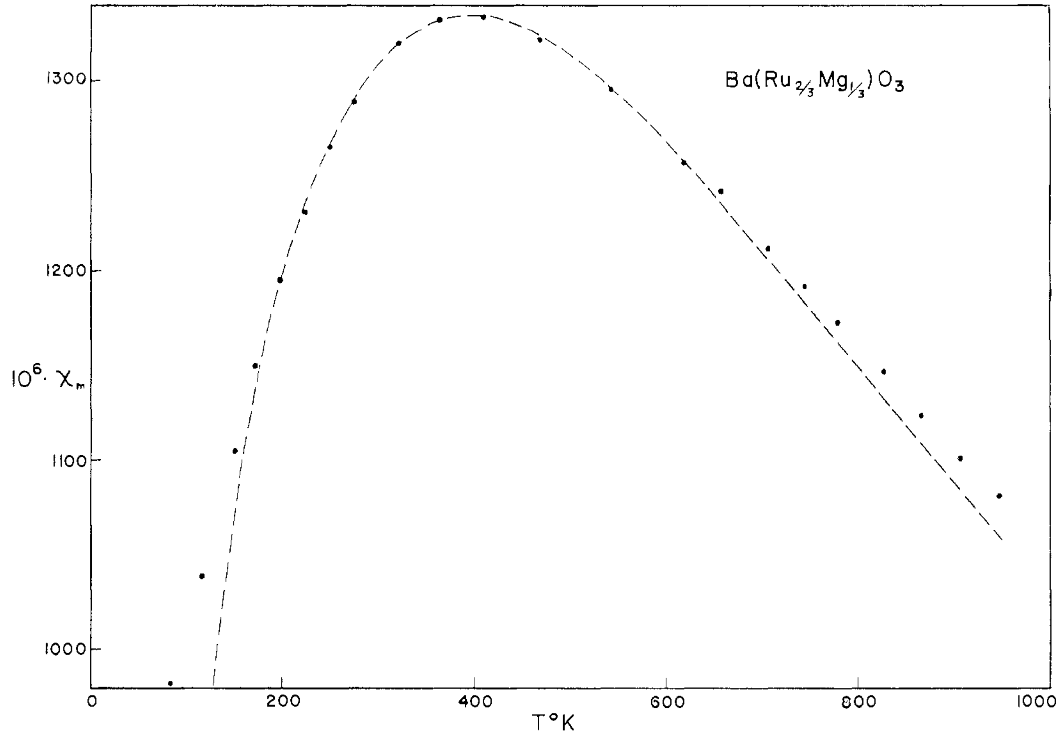

Figure 3.—Comparison of observed and calculated susceptibilities for $Ba(Ru_{2/3}Mg_{1/3})O_3$: ●, observed; – – – –, calculated.

mated to be 20 emu/g leading to a saturation moment of 0.85 BM per ruthenium atom. It is possible, however, that measurements on a single crystal using higher field strengths would lead to a value a little larger than this. The remanence and coercive force were high, being 14 emu/g and ~3000 oersteds, respectively.

$BaRuO_3$.—The over-all susceptibility of this compound is low and rises with temperature to a broad maximum at about 430°K from which it falls off more slowly. High-temperature $1/\chi_m$-T plots did not give straight lines up to the highest temperature studied. The conductivity of a compacted pellet was good at both 77°K and room temperature. Tables I and IV give the magnetic data.

Table IV

Magnetic Susceptibility of $BaRuO_3$

$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K
0.449	78	0.546	240	0.598	506
0.466	119	0.572	292	0.585	612
0.496	165	0.596	361	0.574	682
0.519	199	0.604	426	0.556	765

$Ba(Ru_{2/3}Mg_{1/3})O_3$.—This compound showed a magnetic behavior similar to that of $BaRuO_3$ and the data are plotted in Figure 3. The maximum in the χ_m-T curve is sharper, the temperature of the maximum, about 390°K, is lower, and the over-all susceptibility is higher (Table I). The resistance of a compacted pellet was of the order of ~10^4 ohms-cm, much higher than that of the other materials.

Table V

Magnetic Susceptibility of $Ba(Ru_{2/3}Mg_{1/3})O_3$

$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K
0.982	84	1.320	319	1.212	706
1.038	117	1.333	363	1.192	743
1.105	150	1.335	383	1.173	778
1.150	173	1.334	409	1.147	827
1.195	198	1.322	468	1.124	866
1.232	223	1.296	542	1.101	908
1.265	250	1.257	617	1.081	948
1.289	275	1.242	657		

$(Ba_{5/6}Sr_{1/6})RuO_3$.—Some difficulty was experienced in obtaining a sample of this material free from traces of $SrRuO_3$. The presence of this impurity was easily observed as a field dependence of susceptibility at low temperatures and a sharp increase in susceptibility below 150–160°K. Eventually, after repeated ball-milling and calcining, a sample was obtained which showed no field dependence and no anomaly in χ_m-T. The χ_m-T data for this sample are given in Table VI. The susceptibility is very low and only slightly dependent on temperature. Resistivity measurements on a pellet indicated that the material was a good conductor.

Table VI

Magnetic Susceptibility of $(Ba_{5/6}Sr_{1/6})RuO_3$

$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K
0.769	77	0.689	333	0.610	685
0.754	130	0.667	409	0.595	778
0.737	190	0.647	487	0.580	876
0.715	260	0.627	589	0.568	971

Sr_2RuO_4.—More difficulty was experienced in obtaining this material free from $SrRuO_3$. Even using excess $SrCO_3$ and heating for periods of several weeks, a trace of $SrRuO_3$ was always present. However, the samples which had been heated for a longer time always showed less impurity, and it is likely that all the $SrRuO_3$ could be removed if a sufficiently long heating time were used. The χ_m-T data are given in Table VII and illustrate the anomalous rise at 150°K due to the $SrRuO_3$ impurity. An interesting feature is the constant susceptibility between 260 and 560°K

Table VII

Magnetic Susceptibility of Sr_2RuO_4

$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K	$10^3\chi_m$	T, °K
1.68	77	1.09	197	1.05	563
1.61	101	1.07	251	1.04	610
1.57	116	1.06	330	1.01	716
1.50	130	1.06	402	0.99	807
1.42	138	1.06	462	0.96	883
1.28	149	1.06	512	0.92	982

with only a small reduction beyond that. Room-temperature conductivity measurements on a compacted pellet showed that it was a conductor, but had a higher resistivity than $SrRuO_3$.

Discussion

The formal valence state of ruthenium in all of the compounds considered here is IV (d^4) except for $Ba(Ru_{2/3}Mg_{1/3})O_3$ in which it is V (d^3). The possibility of oxygen deficiencies exists, especially in the magnesium compound for which an analysis showed only 80% of the rutheniums are Ru(V).[4] In the ruthenium(IV) compounds the production of altervalent ions from this source is expected to be quite small, because IV is a particularly stable valence state for this metal.

In the cubic field of the oxygen octahedra the d orbitals are split into an upper e_g doublet and a lower t_{2g} triplet, and it is the experience with ruthenium compounds that this splitting is sufficiently strong to force spin pairing in the t_{2g} levels for electron configurations greater than d^3. The d^4 compounds would then be expected to have two unpaired electrons and the d^3 compound three, giving rise to "spin-only" magnetic moments of 2.83 and 3.87 BM, respectively. Because of the high value of the spin–orbit coupling constant of Ru(IV), "spin-only" values are not to be expected, but nevertheless the high temperature moments for two of the d^4 compounds, $CaRuO_3$ (3.0 BM) and $SrRuO_3$ (2.6 BM), are in fair agreement with these values. In the other compounds Curie–Weiss laws did not hold below 1000°K and it was not possible to measure a μ_{eff} that was independent of temperature.

The high conductivities indicate that all of the electrons cannot be localized. This is certainly true in $SrRuO_3$, which has metallic-type conductivity, and it is likely that this is also the case for the other high-conducting compounds, rather than a hopping-type mechanism involving impurity sites. Thus, the compound in which such sites are present in greatest numbers, $Ba(Ru_{2/3}Mg_{1/3})O_3$, has the highest resistance. To explain the conductivity in $SrRuO_3$, one may note that the perovskite structure is particularly favorable for π overlap between cation t_{2g} and anion p orbitals, and if this overlap were strong enough, a π band and a π^* band would result. Partial occupation of the π^* band could then lead to metallic-type conductivity. The conductivity of RuO_3 has been explained in this way.[7] The low conductivity of $Ba(Ru_{2/3}Mg_{1/3})O_3$ results because the Mg does not have the orbitals available to form a band and isolates the ruthenium atoms into face-shared pairs.

While that explanation is sufficient for the perovskite structure, in the nonperovskites one has to invoke a supplementary mechanism to explain the conductivity across the face-shared octahedra. This is possible if the cation–cation separation across the face is small enough for direct overlap between the cation t_{2g} orbitals, making some electrons collective rather than localized. The Ru–Ru separation in $BaRuO_3$ is 2.55 A and that in $(Ba_{5/6}Sr_{1/6})RuO_3$ is 2.47 A, both being smaller than the corresponding distance in the metal itself (2.65 A) so this direct interaction is possible and is, moreover, further evident in the magnetic behavior.

It is the isolated pairs in $Ba(Ru_{2/3}Mg_{1/3})O_3$ that constitute the simplest system in our magnetic study, and if there is a direct interaction or metal–metal bond between the ruthenium atoms, then it should be apparent from the magnetic properties of this compound. The theory of spin-coupled polynuclear systems has been developed by Kambe,[8] and the observed susceptibility values may be compared with those predicted on the basis of his model for a binuclear system. The interaction between the two metal atoms is written as a perturbation in the total Hamiltonian of the form $H_{1,2} = -2J\mathbf{S}_1\cdot\mathbf{S}_2$, where J is the exchange constant and $\mathbf{S}_1$, $\mathbf{S}_2$ are the spin operators of the coupled atoms. The result for two atoms of spin $^3/_2$ is

$$\chi_A = \frac{g^2N\mu_B{}^2}{3kT}\left[\frac{42 + 15\exp(6x) + 3\exp(10x)}{7 + 5\exp(6x) + 3\exp(10x) + \exp(12x)}\right] + N(\alpha)$$

where $x = -J/kT$ and $N(\alpha)$ is the Van Vleck temperature-independent term. The expression contains three parameters: g, J, and $N(\alpha)$. $N(\alpha)$ is usually small and a value of 60×10^{-6} cgs unit was assumed. The parameters g and J have been adjusted to give the best fit to the data in the region of the maximum in the susceptibility curve. Figure 3 shows the comparison between the observed and calculated magnetic susceptibilities using $g = 1.744$ and $J/k = -129°$. The agreement in the central temperature region is very good, and, considering the extended temperature range covered and the fact that not all of the ruthenium in the compound may be Ru(V), the deviations at the extremes are not too serious. High values at low temperatures are to be expected in any case owing to the inevitable presence of small amounts of uncoupled ruthenium ions. The g value of 1.74 is equivalent to a μ_{eff} of 3.4 BM and implies a rather larger amount of orbital contribution than has been so far found for octahedral d^3 configurations.[9]

It is interesting that the curve for $BaRuO_3$ has a similar shape, although the interactions involved are more complex. In this compound there is a linear cluster of three atoms with two metal–metal interactions; also, each end atom is involved in two metal–oxygen–metal interactions and thus is in a different environment from that of the central Ru atom. The magnetic results seem to indicate that the metal–metal interactions are considerably stronger than those through an oxygen ion and dominate the magnetic properties. Ru(IV)–O–Ru(IV) interactions involving localized electrons are in fact predicted to be only weakly antiferromagnetic.[10] Again with $(Ba_{5/6}Sr_{1/6})RuO_3$ there are competing metal–metal and metal–

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(7) J. B. Goodenough, *Bull. Soc. Chim. France*, 1200 (1965).

(8) K. Kambe, *J. Phys. Soc. Japan*, **5**, 48 (1950).

(9) B. N. Figgis, J. Lewis, and F. E. Mabbs, *J. Chem. Soc.*, 3138 (1961).

(10) J. B. Goodenough, "Magnetism and the Chemical Bond," Interscience Publishers, Inc., New York, N. Y. 1963, p 174.

oxygen–metal interactions, but the susceptibility curve is quite different. There is no maximum and only a small variation in the susceptibility with temperature (25% over 900°). The inference is that the interaction in this compound is considerably stronger than in the others and has not broken down even at the highest temperatures. Significant support to this view is given by the Ru–Ru distance in this compound (2.47 A), which is much shorter than in the others. A difficulty is apparent, however, because the susceptibility increases as the temperature is lowered. There are several explanations which may be invoked to account for this rise, *e.g.*, a proportion of the ruthenium atoms unpaired possibly in surface sites, lack of stoichiometry, or the effect of Sr atoms on some of the rutheniums, but such speculations can only be very tentative at this stage.

The ferromagnetism of $SrRuO_3$ is interesting and rather unexpected. A possible explanation may be that, of the four t_{2g} electrons, it is the ones with β spin that are responsible for the conduction in a narrow π^* band. The action of this β-spin band is to make all of the opposing localized α spins codirectional resulting in ferromagnetism. This model would give a saturation moment of $3 - 1 = 2$ BM if the moments were strictly collinear, but less if they were canted into a spiral. Generally, canted moments resist reversal on reversing the field more than collinear ones and so both the low saturation moment (0.85 BM) and the high coercive force (~3000 oersteds) are consistent with a spiral configuration. This model is compatible with that of Goodenough[11] in which the ferromagnetic metals are accounted for by the simultaneous presence of collective and localized d electrons. The same arguments should also apply to $CaRuO_3$, but no signs of ferromagnetism were found in this material. The explanation may involve the difference in size between Ca and Sr and the corresponding greater distortion in $CaRuO_3$, although the parameters of the orthorhombic unit cell are fairly similar (5.58, 7.77, 5.45 A for $CaRuO_3$ and 5.57, 7.85, 5.53 A for $SrRuO_3$). A more likely possibility is that the strontium d orbitals are involved in band formation in $SrRuO_3$. Ruthenium and strontium are in the same period, and the energies of these orbitals must be comparable. Some preliminary attempts to obtain more information have been made by studying the magnetic properties of $CaRuO_3$–$SrRuO_3$ and $BaRuO_3$–$SrRuO_3$ solid solutions. So far it has been found that the position of the Curie point is not changed by the substitution of up to $^1/_3$ Sr by Ca, or $^1/_4$ Sr by Ba, although the over-all magnetization is diminished. It is possible that not all of the substituted ions are in true solid solution, but in the Ba case, especially, it appears from the X-ray data that most of them are.

The remaining compound, Sr_2RuO_4, contains Ru in a greater state of dilution than the others. Considering that there can be no direct metal–metal interactions in the K_2NiF_4 structure and that any Ru–O–Ru interactions can occur in only two directions with any strength, it is unlikely that the almost temperature-independent susceptibility of this compound is due to magnetic interactions. One might consider the Ru as magnetically dilute and assume the theory of Griffith applies.[12] In this theory octahedral coordination is assumed and a coupling scheme intermediate between Russell–Saunders and j–j coupling is used to calculate the susceptibility. This is necessary for the second and third series transition elements because of their large spin–orbit coupling constants (ζ), and for Os(IV) octahedral complexes, for instance ($\zeta = 4000$ cm^{-1}), temperature-independent susceptibilities of about 1000×10^{-6} cgs unit are predicted and found.[13] For Ru(IV), however, the coupling constant is not so high ($\zeta = 1400$ cm^{-1}) and the susceptibility is expected to remain temperature dependent. This has been found to be the case for complexes such as K_2RuX_6 (X = Cl, Br, I).[13] It appears then that our results are not in accord with this model. A possibility is that the oxygen octahedra in Sr_2RuO_4 are distorted to an extent that would make the theory inapplicable. One of the characteristics of this structure is that four of the octahedral oxygens are shared by two rutheniums whereas the other two are shared by a strontium and a ruthenium, and this must lead to some distortion from cubic symmetry.

It is of interest to mention that the magnetic properties of RuO_2 are also unaccounted for. This compound, which has the rutile structure, has a very low susceptibility which increases slightly with temperature.[14] It was thought until recently that this was due to direct Ru–Ru interactions along the *c* axis. If this were so, the structure would be distorted to give alternate short and long Ru–Ru distances, but the single-crystal study of Cotton and Mague showed that there was no distortion and the Ru–Ru separation along the *c* axis was constant at 3.107 A.[15] Possibly all of the d electrons in this compound are collective, and the material is Pauli paramagnetic.

Acknowledgments.—The saturation magnetization and conductivity of $SrRuO_3$ were measured by W. H. Cloud and J. L. Gillson, respectively, at the Experimental Station, E. I. du Pont de Nemours and Co., Wilmington, Del. Discussions with John B. Goodenough of Lincoln Laboratory, Massachusetts Institute of Technology, Cambridge, Mass., were helpful in interpreting the ferromagnetic behavior of $SrRuO_3$. The support of this research by the National Science Foundation, Grant GP 3461, is gratefully acknowledged.

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[11] See ref 10, pp 297–300.

[12] J. S. Griffith, *Discussions Faraday Soc.*, **26**, 173 (1958).

[13] A. Earnshaw, B. N. Figgis, J. Lewis, and R. D. Peacock, *J. Chem. Soc.*, 3132 (1961).

[14] A. N. Guthrie and L. T. Bourland, *Phys. Rev.*, **37**, 303 (1931).

[15] F. A. Cotton and J. T. Mague, *Inorg. Chem.*, **5**, 317 (1966).