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Magnetic Interactions of Ruthenium, Rhodium, and Iridium in the Hexagonal Barium Titanate Structure

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The magnetic susceptibilities of some quarternary oxides with the hexagonal barium titanate structure have been measured from 77–900°K. These phases correspond to the formulas $Ba_3MTi_2O_9$, $Ba_3M_2MgO_9$, and $Ba_3M_2NiO_9$, where M = Ru or Ir, and to the formula $Ba_3Rh_{0.6}Ti_{2.4}O_9$. Except for $Ba_3Ir_2MgO_9$, which had temperature independent susceptibility, the compounds showed Curie–Weiss behavior with large, negative Weiss constants, indicating considerable magnetic interaction between the magnetic ions. The calculated magnetic moments were in reasonable agreement with theory when these magnetic interactions and the large spin-orbit coupling constants of the 4*d* and 5*d* transition metals were considered. Thus, for Ru(IV) in $Ba_3RuTi_2O_9$ ($\theta = -256°$) $\mu_{\text{eff}} = 2.86\ \mu$B, and for Ir(IV) in $Ba_3IrTi_2O_9$ ($\theta = -408°$) $\mu_{\text{eff}} = 1.76\ \mu$B.

Introduction

Compared to the great quantity of magnetic data available for the ions of the first transition series, relatively few data for the second and third transition series have been published. In order to understand better the magnetic moments and magnetic interactions of some of these heavier metal ions, the magnetic susceptibilities of a number of them have been measured in this laboratory using phases of the perovskite structure and the hexagonal barium titanate (HBT) structure. Some of the results for Ru, Rh, and Ir in the HBT structure are reported here.

The crystal structure of the HBT phase was first determined by Burbank and Evans (*1*). It was later suggested that platinum stabilized the hexagonal phase, and it was found that a number of ions other than platinum may aid in its formation (*2*).

A compound ABO_3 with the HBT structure can be described as having layers of AO_3 in cubic and hexagonal close-packing with the sequence fcc. The oxygen octahedra share corners or faces and two-thirds of the B cations are in face-sharing octahedra, while the other third are in corner-sharing octahedra. The only known A cation for oxides with the HBT structure is Ba. Fluorides are, also, found in the HBT structure with A = Cs, Rb, and Tl (*3*). It has been proposed by Ward and co-workers that the stability of the HBT structure is due to the metal–metal bonding (*4*, *5*). Blasse explained the stability of the structure in terms of the anionic polarization.

Two fluoride systems with the HBT structure have been studied extensively, $RbNiF_3$ and $CsMnF_3$. $RbNiF_3$ has been described as a ferrimagnetic substance with a $T_N = 140°K$ (*6*). The ferrimagnetic ordering would result from the two Ni environments in the HBT structure; the Ni ions in the face-sharing octahedra would have parallel spins while the Ni ions in the corner-sharing octahedra would have an antiparallel spin to the other Ni ions. The Ni was replaced by magnetic and nonmagnetic ions (Cd, Ca, Mg, Co, and Mn) to study further the magnetic structure (*7*). The nonmagnetic ions lowered the Curie temperature more than the magnetic ions. McGuire explained the differences in behavior in terms of site preference of the substituted ions. $CsMnF_3$, on the other hand, was described as an antiferromagnetic substance with a $T_N = 55°K$ (*8*). The antiferromagnetic ordering was explained by assigning antiparallel spins to the Mn ions in the face-sharing octahedra and antiparallel spins to the Mn ions in the corner-sharing positions.

In the work reported below, the magnetic properties of two oxide systems with the HBT structure were investigated. The first system consists

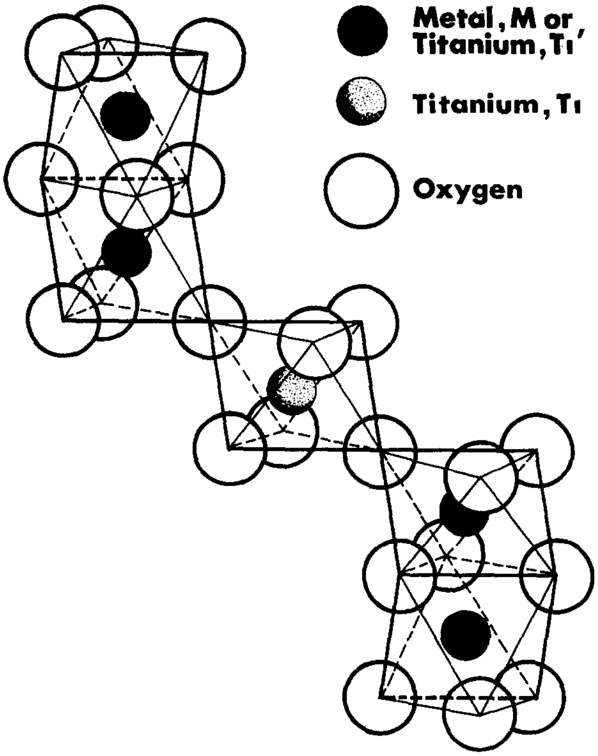

FIG. 1. A portion of the hexagonal barium titanate structure.

of compounds with the general formula $Ba_3MTi_2O_9$, where M = Ru, Ir, or Rh. The second system has compounds with the formula $Ba_3M_2M'O_9$, where M = Ru, Rh, or Ir and M′ = Ni or Mg. The preparations, the structure determinations, and some limited magnetic work were done by Dickinson on the $Ba_3MTi_2O_9$ system (*4*). Dickinson concluded that the paramagnetic metal ions entered the four fold position in the hexagonal structure to the extent of filling one half of the face-shared octahedral positions. This would then allow some metal–metal bonding with the titanium. There is, also, some possibility of long-range, superexchange interactions between the paramagnetic ions through a titanium-oxygen bridge, i.e., Ru–O–Ti–O–Ti′–Ru, Fig. 1 Half of the titanium in the structure would be in face-sharing octahedra, Ti′, and half in corner-sharing, Ti. In this research project the magnetic properties of the $Ba_3MTi_2O_9$ system were studied over the temperature range, 77–900°K. The Rh analog was studied with variations in composition, Rh–Ti.

The preparations and structure determinations of $Ba_3Ru_2M'O_9$, where M′ = Ni or Mg, were done by Donohue (*9*). The Ru ions were found to be in the face sharing octahedra with the Ru–Ru distance 2.63 Å, while the Mg or Ni ions were in the corner-sharing octahedra. $Ba_3Ru_2MgO_9$ is antiferromagnetic with $T_N = 390°K$ (*10*). As described below, the magnetic properties of the Ni analog have now been measured and are compared to those of the Mg compound. The Ir compounds were also prepared and their magnetic properties are reported. The attempts to prepare the Rh analogs were not successful.

Experimental Section

Preparation Techniques

The reactants were weighed on an analytical balance and then mixed thoroughly in an agate mortar. They were placed in a combustion boat and heated in air in a Harper electric furnace at the desired temperature for 24 hr. The powder pattern of the sample was then checked with an X-ray diffractometer to determine if further heatings were necessary to obtain the hexagonal phase.

$Ba_3MTi_2O_9$ System, M = Ir, Ru, Rh

Barium carbonate, the metal, and titanium dioxide were weighed to make the compound with the desired composition. When M = Ru or Ir the desired phase was obtained using the preparation method of Dickinson (*11*). When M = Rh the powder pattern indicated a number of shoulders and extra peaks, in addition to the dominant peaks of the HBT spectrum.

Other compositions of Rh were tried, and when the Rh–Ti ratio was increased to $Ba_3Rh_{1.5}Ti_{1.5}O_9$ the diffraction pattern showed an increase in intensity of the extra peaks and shoulders. With a decrease to $Ba_3Rh_{0.6}Ti_{2.4}O_9$ the X-ray pattern was that of the HBT structure, but when the Rh composition was further decreased to $Ba_3Rh_{0.3}Ti_{2.7}O_9$ a much more complex X-ray pattern resulted. The HBT pattern still remained but many other peaks were present, and they could not be indexed in terms of the starting materials or $BaTiO_3$.

$Ba_3M_2MgO_9$ System, M = Rh, Ir

Iridium metal reacted with the appropriate ratios of barium carbonate and magnesium carbonate yielding a compound having an X-ray pattern similar to that of the ruthenium analog prepared by Donohue (*9*). The mixture was heated in pellets for 12 hr at 1000°C, then for two 12-hr periods at 1100°C. The diffraction pattern showed slightly smaller 2*θ* values than that of the ruthenium analog.

Rhodium metal reacted with the appropriate ratios of barium carbonate and magnesium carbonate. The resulting composition had an X-ray pattern unlike that of a typical HBT structure.

$Ba_3M_2NiO_9$ System, M = Rh, Ir, Ru

Ruthenium metal reacted with the appropriate ratios of nickel carbonate and barium carbonate yielding a compound having the same X-ray pattern as the Mg analog. The mixture was heated for 12 hr at 1000°C, then for another twelve hours at 1100°C.

The diffraction pattern of the Ir analog showed extra peaks, and attempts to eliminate the impurity by varying the temperature and the time of the preparations did not result in significant improvement of the pattern. A mixture of Rh with the appropriate ratios of barium carbonate and nickel (II) carbonate was heated in the same manner as for the Mg analog and the product gave an X-ray pattern similar to that of the Mg compound.

X-Ray Diffraction Data

Powder diffraction data were obtained with a General Electric XRD-5 diffractometer, using Ni-filtered copper Kα radiation. The X-ray patterns of all samples were obtained for 2θ values from 10–90° and these patterns were used to confirm the presence of the HBT structure.

Magnetic Measurements

Magnetic susceptibilities were measured on an enclosed Gouy balance from 77–600°K. Some of the susceptibility measurements were repeated on small samples in a Faraday magnetic balance. To check for field dependency measurements were made at four field strengths, ranging from 497–6883 Oe. The field calibrations were made using $HgCo(SCN)_4$ with $\chi_g = 16.44 \times 10^{-6}$ c.g.s. units at 293°K and $\theta = -10°$ (*12*). For the high temperature calibration Gd_2O_3 was used as the standard with $\chi_g = 135 \times 10^{-6}$ c.g.s. units at 293°K and $\theta = -18°$ (*13*). The molar susceptibilities were corrected for diamagnetism using the values in Selwood. The details of the measurements at low and high temperatures and the estimated errors in the susceptibilities, about ±5% overall, are as reported previously (*10*).

Results and Discussion

The t_{2g}^4 configuration frequently gives low magnetic moments at room temperature because of a large value of the spin-orbit coupling constant, λ. Thus for a $5d^4$ ion, like Ir(V), the moment would be near 1.3 μB at 300°K and the susceptibility would be temperature independent (*14*, *15*). The spin-orbit coupling constant is -2750 cm^{-1} for Ir(V). The moment for Ru(IV) is expected to be close to 2.8 μB since the spin-orbit coupling constant is -700 cm^{-1}. The μ_{eff} for Ru(IV) was found to be 2.9 μB at 293°K and to fall with temperature in the compounds K_2RuF_6, K_2RuCl_6 and K_2RuBr_6 (*16*). However, the susceptibility of $Ru(dipy)Cl_4$ showed Curie–Weiss behavior; Figgis explained this in terms of the distortion from octahedral symmetry with the introduction of the dipyridyl group (*17*).

The t_{2g}^3 configuration is expected to have moments that are independent of temperature and reduced from the spin-only value by the factor $(1 - a\lambda/10Dq)$; thus the Ru(V) ion which has a λ value of 500 cm^{-1} should have a μ_{eff} of about 3.5 μB. Some Ru(V) compounds with the general formula $M(I)RuF_6$ have μ_{eff} values ranging from 3.48–3.70 μB (*18*).

The t_{2g}^5 configuration results in moments slightly dependent on the temperature at high values of λ. The spin-orbit coupling constants for Rh(IV) and Ir(IV) are -1600 cm^{-1} and -5000 cm^{-1} and the moments expected are about 2.0 and 1.8 μB, respectively. The system M_2RhF_6, where M = K, Rb, or Cs, has moments at room temperature between 1.96–2.01 μB, and they are temperature dependent (*19*).

The $Ba_3MTi_2O_9$ Phases

In Table I are summarized the magnetic data for the $Ba_3MTi_2O_9$ system, where M = Rh, Ru, or Ir. $Ba_3RuTi_2O_9$ has a normal moment, 2.86 μB, and the susceptibility follows the Curie–Weiss law above 150°K. The Curie–Weiss behavior may be a result of distorted octahedra in the HBT structure. Below 150°K a Curie–Weiss law behavior was found for $Ba_3RuTi_2O_9$ but with the $1/\chi'_M$ vs T curve having a

TABLE I

MAGNETIC DATA FOR $Ba_3MTi_2O_9$ PHASES

	$-\chi_{dia} \times 10^6$	$\chi'_M \times 10^6$ (at 293°K)	θ °K	μ_{eff} μB^a
$Ba_3IrTi_2O_9$	193^b	555	−408	1.76
$Ba_3Rh_{0.3}Ti_{2.7}O_9$	223	1674	−50	1.8–2.1
$Ba_3Rh_{0.6}Ti_{2.4}O_9$	227	1157	−140	1.8–2.0
$Ba_3RhTi_2O_9$	232	927	−220	1.8–2.0
$Ba_3Rh_{1.5}Ti_{1.5}O_9$	239	593	−504	1.94
$Ba_3RuTi_2O_9$	232	1858	−256	2.86

[a] Calculated by using the equation: $\mu_{eff} = 2.83\sqrt{\chi'_M(T - \theta)}$.

[b] 50×10^{-6} c.g.s. TIP included.

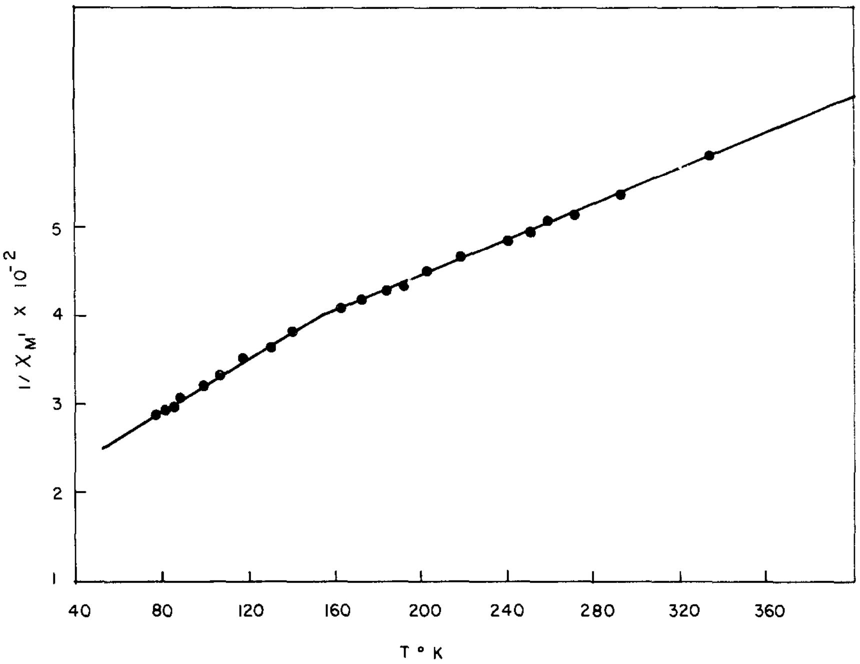

FIG. 2. The reciprocal of the molar susceptibility versus temperature for $Ba_3RuTi_2O_9$.

steeper slope, Fig. 2. Whether this abrupt change of slope is due to a phase change or to some other factor has not been determined yet.

The $Ba_3IrTi_2O_9$ compound has a moment of 1.76 μB in good agreement with the predicted 1.8 μB. A correction for temperature independent paramagnetism, TIP, of 50×10^{-6} c.g.s. units was made in the χ'_M values resulting in a straight line for the graph of $1/\chi'_M$ vs T, Fig. 3. Cooke et al., used a TIP correction of 290×10^{-6} c.g.s. units for Ir(IV) in magnetic studies of $(NH_4)_2IrCl_6$ and K_2IrCl_6 (*20*). If that TIP correction were used, the moment would be reduced to 1.17 μB at 293°K and it would vary with temperature. If no TIP correction were used, the calculated moments would vary from 1.60–2.11 μB over the temperature range 77–293°K.

The Rh(IV) analog was studied with variations in composition of Rh–Ti. The X-ray powder pattern

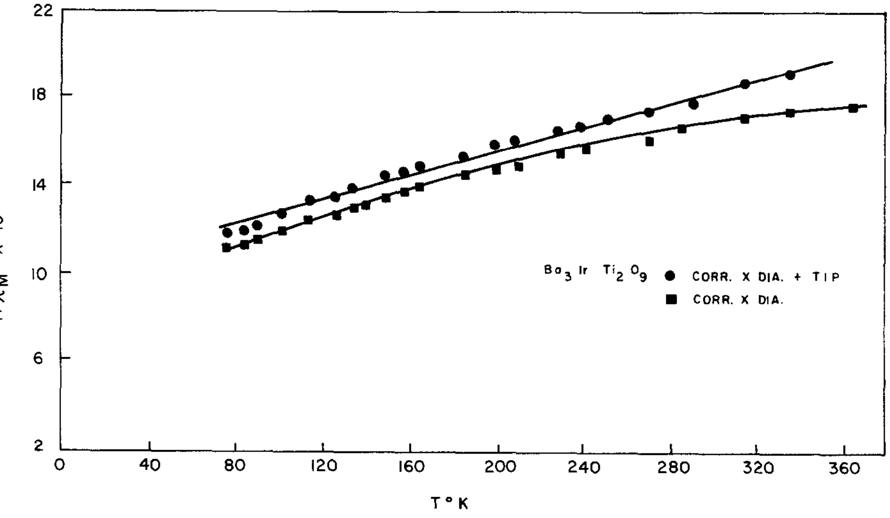

FIG. 3. The reciprocal of the molar susceptibility versus temperature for $Ba_3IrTi_2O_9$.

corresponded to that of an HBT structure when the composition was $Ba_3Rh_{0.6}Ti_{2.4}O_9$. The Weiss constant, θ, increases as the Rh composition increases. There is some deviation from Curie–Weiss law behavior below 100°K. The values of μ_{eff} vary from 1.8 μB at 77°K to 2.1 μB at 293°K, Table I.

For the system, $Ba_3MTi_2O_9$, Dickinson concluded that the paramagnetic ions, M, were in the face-shared octahedra, but his calculations did not indicate how the M ions were arranged in these positions (*4*). The magnetic interactions would be determined by the arrangement of the M ions, by the electron configuration of the M ions, and by the strength of any exchange interaction with neighboring ions. In order to discuss these magnetic interactions in the $Ba_3MTi'TiO_9$ system, a more detailed description of the HBT structure follows in which it is assumed that there is either M or Ti′ ion in each face-shared octahedron and Ti in the corner-shared octahedron, Fig. 1. The M ion can be considered in terms of its interactions with three types of paramagnetic neighboring ions: (1) six neighbors in the same layer with connections through M–O–Ti–O–M with a 90° angle at Ti; (2) three neighbors in a plane above with connections M–O–Ti–O–M and 180° angles at Ti; (3) three more neighbors in the same plane above but connected through M–O–Ti–O–M with a 90° angle at Ti.

The strongest interactions are considered to be the long-range superexchange through the 180° M–O–Ti–O–M connection, which as suggested by Blasse would be an antiferromagnetic interaction (*21*). Within the layers there could then be ferromagnetic coupling through the 90° M–O–Ti–O–M interaction using two *d* orbitals of the Ti ion. Thus within the layers the spins could be coupled ferromagnetically and there could be antiferromagnetic interaction between the layers to effect a net antiferromagnetic interaction in agreement with the negative intercepts of $1/\chi'_M$ vs *T*.

If the M ions were paired in the face-shared octahedra, the M ion with the larger number of half-filled orbitals should interact more strongly. This arrangement of the M ions can be discounted on the basis of the magnetic measurements since the Ru(IV) should then have shown the strongest antiferromagnetic coupling. As discussed below for the $Ba_3M_2M'O_9$ phases where the paramagnetic ions *are* in both of the face-shared octahedra, the Ru compounds do show the strongest interaction.

The $Ba_3M_2MgO_9$ and $Ba_3M_2NiO_9$ Phases

In the system $Ba_3M_2M'O_9$, where M = Ru or Ir and M′ = Mg or Ni, the M ion is in all of the face-shared octahedra (*9*). This permits, in addition to the long-range, superexchange interactions, M–O–Ti–O–M, the 90° interactions, M–O–M, between M ions in the face-shared octahedra, leading to ferromagnetism for the electron configurations involved here. Also, direct overlap of the *d* orbitals, metal–metal interaction, leading to antiferromagnetic behavior may be present. The data are summarized in Table II.

The Ir(V) system seems to be a relatively simple one in terms of the magnetic behavior. The χ'_M values for the $Ba_3Ir_2MgO_9$ compound were almost independent of temperature with a value of 700 × 10^{-6} c.g.s. units at 293°K. This agrees well with the TIP value of 600 × 10^{-6} c.g.s. units predicted by Figgis and the reported values, which are between

TABLE II

MAGNETIC DATA FOR THE $Ba_3M_2MgO_9$ AND $Ba_3M_2NiO_9$ PHASES

	$-\chi_{dia} \times 10^6$	$\chi'_M \times 10^6$ (at 293°K)	θ °K	μ_{eff} μB
$Ba_3Ir_2MgO_9$	247	700[a]	TIP	1.28 (293°)
$Ba_3Ir_2NiO_9$	256	5210	Not Curie–Weiss	
$Ba_3Ir_2NiO_9$	256	3810[b]	−1	2.99[b]
$Ba_3Ru_2MgO_9$[c]	233	1305	(−1200) (T_N = 390°K)	
$Ba_3Ru_2NiO_9$	242	9758		
$Ba_3Ru_2NiO_9$[d]	242	2974	−242	3.57[d]

[a] Per g-atom of Ir.

[b] Per g-atom of Ni (Ir subtracted out).

[c] Measurements by Callaghan (*10*).

[d] Per g-atom of Ru (Ni subtracted out).

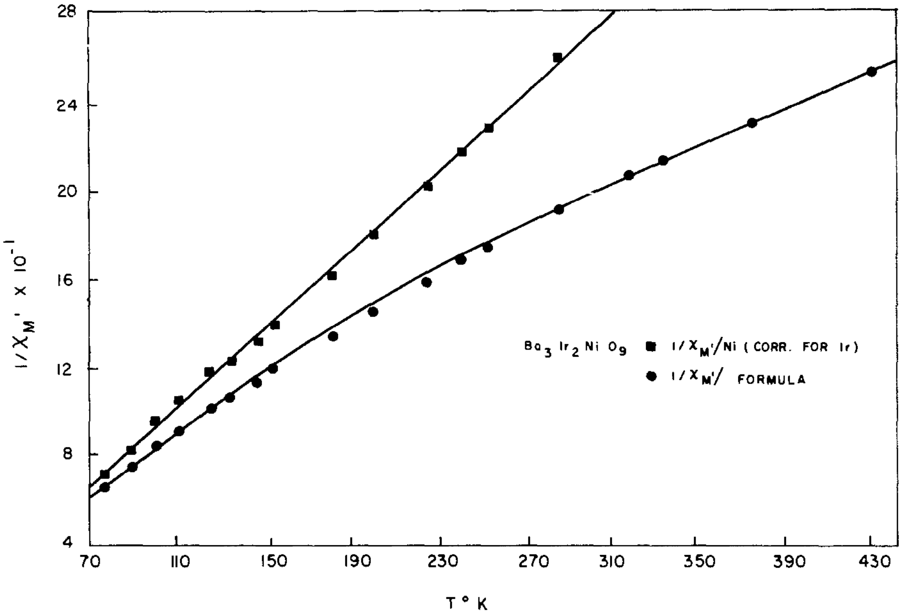

FIG. 4. The reciprocal of the molar susceptibility versus temperature for $Ba_3Ir_2NiO_9$ and the inverse susceptibility per g-atom of Ni(II).

640–730 × 10^{-6} c.g.s. units (*14*). At the lower temperatures there is some increase in χ'_M suggesting that a transition temperature might be found below 77°K.

The data for $Ba_3Ir_2NiO_9$ indicate a large TIP contribution to the susceptibility, Fig. 4. The assumption tested was that all of the TIP contribution was due to Ir(V) with a susceptibility of 700 × 10^{-6} c.g.s. units as found in the Mg analog. When this correction was made, a straight line resulted for $1/\chi'_{N_i}$ vs T with a very small θ, about −1°, Fig. 4. The value then obtained, $\mu_{\text{eff}} = 2.99$ μB, is within the range of moments found for octahedral Ni(II). Thus, it is concluded that the Ir(V) behavior is the same in the Ni and Mg compounds.

$Ba_3Ru_2MgO_9$ is antiferromagnetic with a Néel temperature, T_N, of 390°K (*10*). The high value of T_N made it difficult to determine a value for θ and μ_{eff}, but the data indicate that the Weiss constant would be very negative (about −1200°). For the compound $Ba_3Ru_2NiO_9$ both Ni(II) and Ru(V) may contribute to the susceptibility of the compound. Two methods were attempted to estimate the contribution of each of the paramagnetic ions to the susceptibility. One method was to assume that the χ'_M value for Ru(V) at 900°K in the Ni analog is the same as that for Ru(V) in the Mg compound. This resulted in a calculated μ_{eff} of about 3.8 μB for the Ni(II) ion which is unacceptably high for Ni(II) in an octahedral environment. In the second method it was assumed that the Ni(II) moment lies in the normal range between 2.9–3.3 μB as it does in the Ir compound. The value of 2.99 μB was used for Ni(II), and the moment calculated for Ru(V) was 3.57 μB, which is in good agreement with the theoretical 3.5 μB.

Below 290°K a dip is observed in the curve of $1/\chi'_M$ vs T, Fig. 5. When the susceptibility due to Ni(II) is subtracted from χ'_M, the data indicate an antiferromagnetic interaction with $T_N = 95$°K, Fig. 6. The lower T_N for the Ni case compared to the 390°K found for the Mg compound indicates that there is a decreased amount of metal–metal interaction although in both compounds the Ru-Ru distance is about 2.63Å (*9*). The decrease could be the result of the higher electronegativity of Ni compared to Mg, 1.91 vs 1.31, which would decrease the electron density around the Ru(V) ions. The data for the Ni compound could not be fitted to a calculated curve for a spin-coupled binuclear system with any reasonable values of g, the spectroscopic splitting factor, and J, the exchange integral, as was done for the Mg compound (*10*).

An alternative interpretation of the data would be that the plot of $1/\chi'_M$ versus T indicates the appearance of a ferromagnetic inflection as the temperature is lowered to about 280°K and this is followed at still lower temperatures by an antiferromagnetic trend. Goodenough has predicted a moderate ferromagnetic interaction between a d^3 and a d^8 ion,

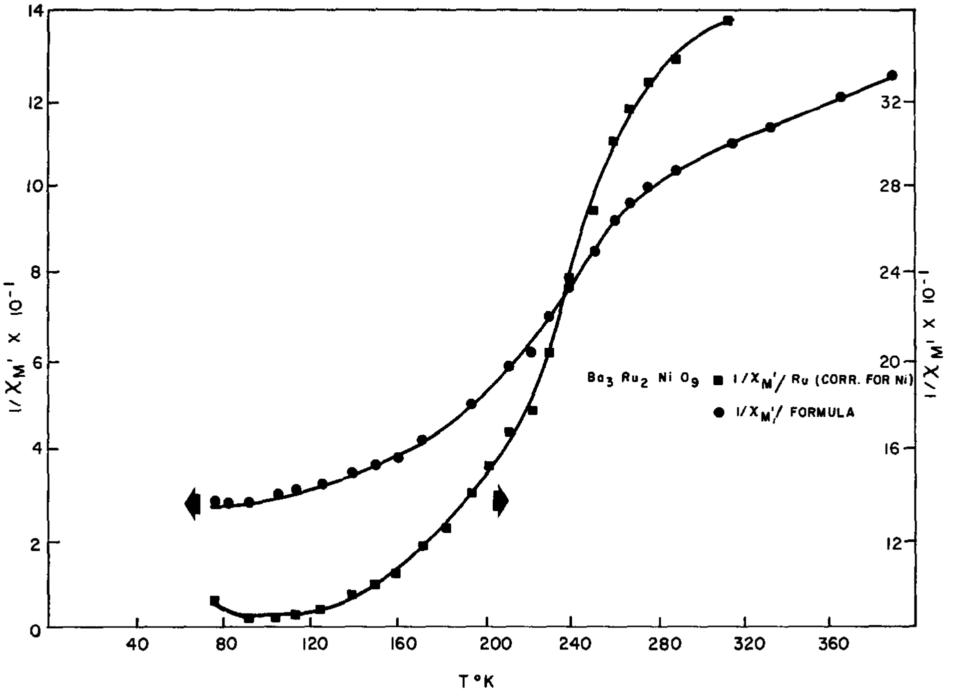

FIG. 5. The reciprocal of the molar susceptibility versus temperature for $Ba_3Ru_2NiO_9$ and the inverse susceptibility per g-atom of Ru(V).

such as Ru(V)-O-Ni(II) (*22*). This coupled with the antiferromagnetic interaction between the Ru(V) ions could lead to the antiferromagnetic susceptibilities at lower temperatures.

In comparing the Ir(V) and Ru(V) ions in the $Ba_3M_2M'O_9$ systems the direct metal-metal interactions were stronger for the Ru(V) ions than for the Ir(V). This could result from the fact that Ru(V)

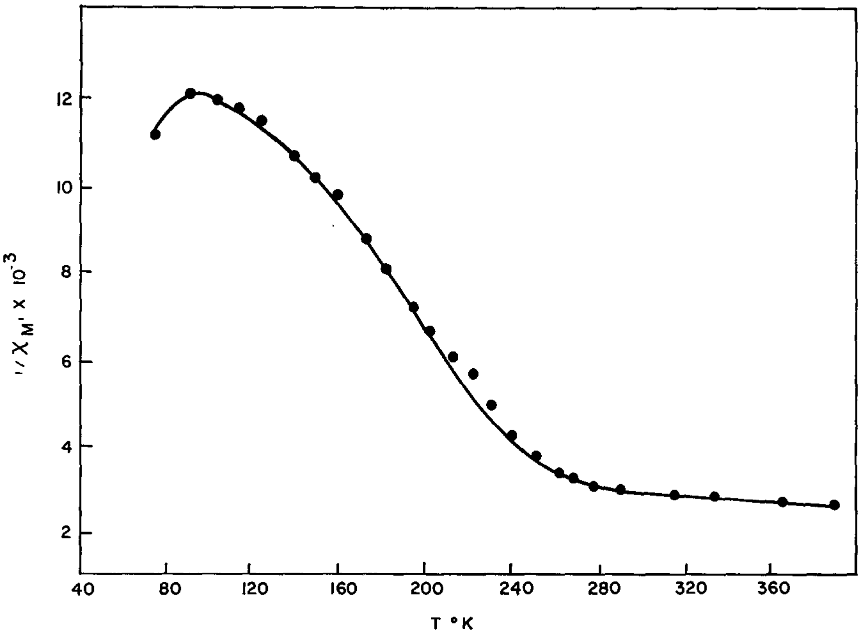

FIG. 6. The molar susceptibility versus temperature of $Ba_3Ru_2NiO_9$ corrected for the susceptibility of Ni(II), i.e., χ'_{Ru}.

ions each have three half-filled t_2/ orbitals available for the overlap through the shared face, while each Ir(V) has only two half-filled orbitals. This is in contrast to the $Ba_3MTi_2O_9$ systems where the antiferromagnetic effects are accounted for by long-range, superexchange interactions and the large Ir(IV) ions have the stronger interactions.

Acknowledgment

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