A Study of the New Cubic, Ordered Perovskites BaLaMRuO$_6$ (M = Mg, Fe, Co, Ni, or Zn) and the Related Phases La$_2M$RuO$_6$ (M = Mg, Co, Ni, or Zn) by ^{99}Ru Mössbauer Spectroscopy and Other Techniques

INMACULADA FERNANDEZ, ROBERT GREATREX, AND
NORMAN N. GREENWOOD*

*Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds
LS2 9JT, England*

^{57}Fe and ^{99}Ru Mössbauer spectroscopy, coupled with magnetic susceptibility measurements down to 4.2 K, have been used to study the electronic and magnetic properties of the new cubic-ordered perovskites BaLaMRuO$_6$ (M = Mg, Fe, Co, Ni, or Zn). The ruthenium is present in the +5 oxidation state in all the compounds except BaLaFeRuO$_6$ which contains iron(III) and ruthenium(IV). All the compounds exhibit long-range antiferromagnetic order, with Néel temperatures in the range 20–40 K. Mössbauer spectra for the new compound La$_2$CoRuO$_6$ and the isostructural cubic perovskites La$_2M$RuO$_6$ (M = Mg, Ni, or Zn) confirm the presence of ruthenium(IV) in these phases and indicate that they are not ordered magnetically at 4.2 K.

Introduction

Until very recently the only oxides known to contain ruthenium in the pentavalent state were the hexagonal perovskite-type phases Ba$_3M$Ru$_2$O$_9$ (M = Mg or Ni) (*1*). However, this situation has now altered and with the aid of ^{99}Ru Mössbauer spectroscopy we have confirmed the presence of ruthenium(V) in several new oxide phases including the ternary perovskites SrFe$_x$Ru$_{1-x}$O$_{3-y}$ (*2*) and the sodium ruthenium oxides Na$_3$RuO$_4$ and Na$_4$Ru$_2$O$_7$ (*3*). Encouraged by the variety of interesting magnetic properties displayed by these materials (*2–4*) we have continued these studies and now report measurements on the new perovskites BaLaMRuO$_6$ (M = Mg, Fe, Co, Ni, or Zn) prepared recently by Darriet and co-workers in Bordeaux (*5*). These compounds crystallize with the cubic,

ordered perovskite structure, which is ideal for studying 180° magnetic superexchange interactions between ruthenium and other metal cations. We also present ^{99}Ru Mössbauer spectra for the closely related new compound La$_2$CoRuO$_6$ and the isostructural compounds La$_2M$RuO$_6$ (M = Mg, Ni, or Zn). After the completion of this work Donohue and McCann reported the preparation of some novel automobile emission control catalysts of formula M_2LnRuO$_6$ (M = Ba or Sr, Ln = Y, rare earth, or Bi), some of which crystallize with the cubic, ordered perovskite structure (*6*). We have confirmed the presence of magnetically ordered ruthenium(V) both in these compounds and in the new calcium analogs Ca$_2Ln$RuO$_6$ (Ln = Y, La, or Eu), and have reported the results elsewhere (*7*).

Experimental

The compounds $BaLaMRuO_6$ ($M = Mg$, Fe, Co, Ni, or Zn) and La_2CoRuO_6 were synthesized by Darriet and co-workers (5), and we are grateful to them for supplying us with samples together with unpublished crystallographic and magnetic susceptibility data. The compounds La_2MRuO_6 ($M = Mg$, Ni, or Zn) were prepared by us using methods described in the literature (8) and were characterized by X-ray powder diffraction using a Philips powder diffractometer.

The Mössbauer spectra were recorded using techniques described previously (3), and computed using programs developed by Dr. T. C. Gibb. The ^{99}Ru chemical isomer shift data are quoted relative to an absorber of natural ruthenium metal at 4.2 K and of thickness 140 mg cm^{-2}. The experimental linewidths of the radioactive sources measured against this absorber were found to be 0.25 ± 0.01 mm sec^{-1}. Sample thicknesses for ^{99}Ru spectra were typically 400 mg cm^{-2} of compound. The ^{57}Fe spectra were recorded using a source of ^{57}Co in a rhodium matrix, supplied by the Radiochemical Centre, Amersham; chemical shifts are quoted relative to the centroid of the spectrum of iron metal at room temperature.

Crystallographic Data

The compounds $BaLaMRuO_6$ ($M = Mg$, Co, Ni, or Zn) crystallize with the face-centered cubic, ordered perovskite structure for which the space group is $Fm3m$ (5). From Table I it can be seen that there is an excellent linear relationship between the lattice parameter and the ionic radius of the divalent metal cation M^{II}, which is good evidence for the formulation of these compounds as $Ba^{II}La^{III}M^{II}Ru^VO_6$. The iron analog is also a cubic perovskite but in this case there is no evidence for cation ordering on the B-site. Moreover, the doubled cell

TABLE I

CRYSTALLOGRAPHIC DATA FOR THE PHASES
$BaLaMRuO_6$

Phase	Cell parameter, a (pm)	Ionic radius $(M^{II})^a$ (pm)
$BaLaMgRuO_6$	795.7	72.0
$BaLaCoRuO_6$	797.0	73.5
$BaLaNiRuO_6$	793.5	70.0
$BaLaZnRuO_6$	798.2	74.5
$BaLaFeRuO_6$	397.3	77.0

^{a} Taken from R. D. Shannon and C. T. Prewitt, *Acta Crystallogr.* B **25**, 925 (1969).

parameter for $BaLaFeRuO_6$ falls off the line, indicating that this compound is unlikely to contain Fe^{II}.

The lattice parameters for the cubic perovskites La_2MRuO_6 ($M = Mg$, Ni, or Zn) have been published previously (8). It should be noted that the lattice type for these compounds is simple cubic and not face-centered cubic as it is for the ordered $Ba_2M^{II}Ru^VO_6$ compounds; the space group is probably $P4_232$.

Magnetic Susceptibility

The magnetic susceptibility was measured for $BaLaCoRuO_6$ down to 4.2 K with a Faraday balance, and the plot of $1/\chi'_M$ vs T for this compound is compared in Fig. 1 with data (5) for the compounds $BaLaMRuO_6$ ($M = Mg$, Fe, Ni, or Zn); all the compounds are antiferromagnetic with Néel temperatures in the range 20–40 K. The Mg, Ni, and Zn compounds were measured to very high temperatures and are seen to follow a Curie–Weiss law in this region. The moments of 3.85 and 3.84 μ_B for the ruthenium ions in $BaLaMgRuO_6$ and $BaLaZnRuO_6$ are very close to the spin-only value of 3.87 for the $(t_{2g})^3$ configuration, and we have observed similar values in the closely related oxides Ca_2YRuO_6, Ca_2LaRuO_6, and Ba_2LaRuO_6 (7). This is perhaps surprising as this
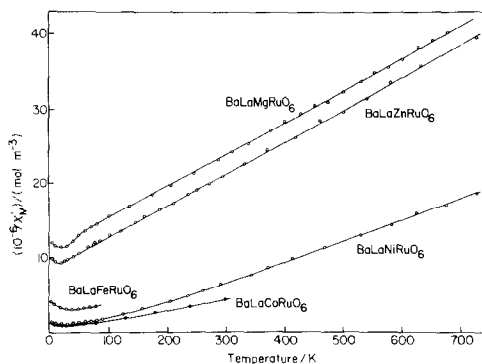
FIG. 1. Plot of the reciprocal molar susceptibility against temperature for the cubic, ordered perovskites BaLaMRuO₆ (M = Mg, Fe, Co, Ni, or Zn).

configuration is expected to have moments that are reduced from the spin-only value by the factor $(1 - \alpha\lambda/10\,\mathrm{Dq})$, where α is 4 for the A_2 ground term and λ has a value of 500 cm^{-1} for Ru^V (9). Thus Ru^V should have μ_{eff} of about 3.5 μ_B, and values ranging from 3.48 to 3.70 μ_B have been observed in the compounds M^IRu^{V}F₆ (10). In order to calculate the moment for Ru^V in BaLaNiRuO₆, the Ni^{II} contribution has been subtracted out assuming a value of 2.99 for μ_{eff}. This gives $\mu_{\mathrm{eff}} = 3.67$ for Ru^V which is very close to the expected value. The Co compound also appears to show Curie–Weiss behavior, but measurements were made only up to 300 K for this compound and this may limit the accuracy of the molar Curie constant, C_M, and the paramagnetic Curie temperature, θ, calculated from the linear portion of the curve. In any case θ is not a reliable measure of magnetic interactions in the Co^{II} compound, owing to spin–orbit effects (11).

Mössbauer Measurements

The ^{99}Ru Mössbauer spectra at 4.2 K for the compounds BaLaMRuO₆ (M = Mg, Co, Ni, or Zn) are very similar to one another, and a representative example is shown in Fig. 2. The spectrum features a magnetic hyperfine pattern in which the 18 components resulting from the $I_g = \frac{5}{2} \rightarrow I_e = \frac{3}{2}$
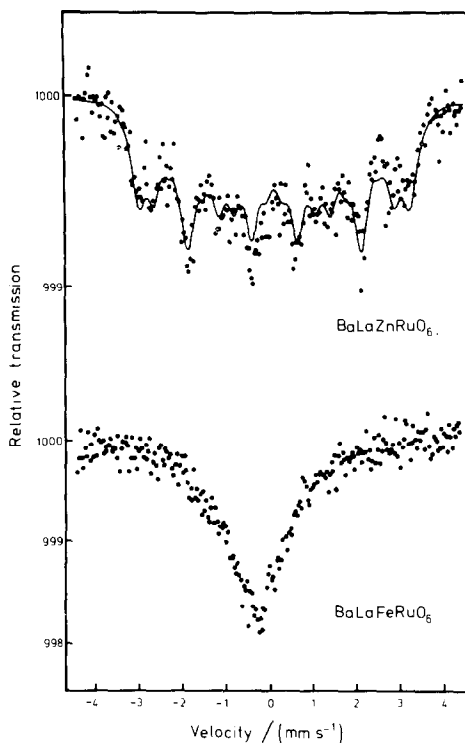

FIG. 2. ^{99}Ru Mössbauer spectra at 4.2 K for BaLaZnRuO₆ and BaLaFeRuO₆. The computed values of the baseline are 67.1×10^6 and 67.2×10^6, respectively.

transition are nearly all distinguishable. The solid line through the data points is the computed least-squares fit in which the relative intensities have been constrained to their theoretical values.

The computed parameters for all the compounds are given in Table II and confirm the presence of magnetically ordered Ru^V in these four compounds. The chemical isomer shifts and magnetic flux densities fall in the narrow ranges +0.04–0.13 mm sec^{-1} (relative to Ru metal) and 55.8–58.4 T, respectively, which are typical for this oxidation state. For example, the magnetically ordered Ru^V oxides Sr₂FeRuO₆ (δ +0.116 mm sec^{-1}, B 52.9 T) (2), Na₃RuO₄ (δ +0.039 mm sec^{-1}, B 58.58 T) (4), and M_2LnRuO₆ [(M = Ca, Ln = Y, La, or Eu; M = Sr, Ln = Y; M = Ba, Ln = La or

TABLE II

^{99}Ru Mössbauer Parameters at 4.2 K for the Perovskites BaLaMRuO$_6$

Phase	Chemical isomer shift, δ^a (mm sec^{-1})	Magnetic flux density, B (T)	Linewidth, Γ (mm sec^{-1})	$\chi^2(d)^b$
BaLaMgRuO$_6$	$+0.131 \pm 0.010$	55.5 ± 0.3	0.45 ± 0.03	280 (241)
BaLaZnRuO$_6$	$+0.095 \pm 0.010$	55.5 ± 0.5	0.40 ± 0.02	172 (241)
BaLaCoRuO$_6$	$+0.040 \pm 0.030$	58.4 ± 0.4	0.29 ± 0.01	153 (241)
BaLaNiRuO$_6$	$+0.063 \pm 0.010$	55.8 ± 0.2	0.40 ± 0.02	564 (242)
BaLaFeRuO$_6$	-0.342 ± 0.020	ca. 14.8 ± 0.3	0.4^c	433 (242)

^{a} Relative to ruthenium metal.
^{b} d = Degrees of freedom.
^{c} Fixed parameter. See comments in text.

Eu) (δ +0.13–0.18 mm sec^{-1}, B 56.1–59.5 T)] (7) all give small positive chemical isomer shifts, and magnetic flux densities in the region of 55 T. As discussed elsewhere (2,4,7) the $(t_{2g})^3$ configuration of Ru^V with $S = \frac{3}{2}$ is expected to generate magnetic fields which are relatively insensitive to changes in environment, and this is borne out in practice. The computed linewidths, which range from 0.29 to 0.45 mm sec^{-1}, are reasonably narrow but are nevertheless broadened slightly compared with the natural linewidth for the source. This may indicate the presence of a small range of hyperfine fields caused by randomization of the Ba^{II} and La^{III} cations on the A-sites.

From Fig. 2 it can be seen that the ^{99}Ru Mössbauer spectrum of BaLaFeRuO$_6$ is quite different from those of the other compounds. It consists of a magnetically broadened resonance centered at -0.34 mm sec^{-1}, indicative of Ru^{IV}. Attempts to curve-fit the spectrum with a single hyperfine pattern have proved unsuccessful. Instead there appears to be a range of Ru environments, consistent with randomization of the Ru and Fe on the B-sites as well as of the Ba and La on the A-sites, coupled with the greater sensitivity of the Ru^{IV} $(t_{2g})^4$ hyperfine field to change in environment. The average value for the flux density of

14.8 T shown in Table II was given by a fit in which the linewidth was constrained to a value of 0.4 mm sec^{-1}. For comparison the Ru^{IV} oxide SrRuO$_3$ gives a flux density of 35.2 T and a chemical isomer shift of -0.33 mm sec^{-1} (12). It appears, therefore, that the spectrum of BaLaFeRuO$_6$ is showing an inward collapse of the magnetic hyperfine splitting indicative of a reduced exchange interaction at the ruthenium similar to that observed in the metallic solid-solutions Ca$_x$Sr$_{1-x}$RuO$_3$ (13) and La$_x$Sr$_{1-x}$RuO$_3$ (14). Alternatively, the small value for the field could indicate the presence of a component of opposite sign transferred from Fe to Ru, though this does not seem to occur to any appreciable extent in the compounds BaLaMRuO$_6$ (M = Co or Ni), where the full Ru^V hyperfine field is observed, despite the coexistence of another magnetic ion on the B-site.

The presence of Ru^{IV} in BaLaFeRuO$_6$ implies the coexistence of Fe^{III} on the B-site, and this has been confirmed by ^{57}Fe Mössbauer spectroscopy. The spectra are shown in Fig. 3 and the computed parameters listed in Table III. At 290 and 100 K the spectra consist of quadrupole doublets ($\Delta = 0.49$ mm sec^{-1}) centered at $+0.40$ and $+0.51$ mm sec^{-1}, respectively, which are typical for high-spin Fe^{III}. The linewidths are
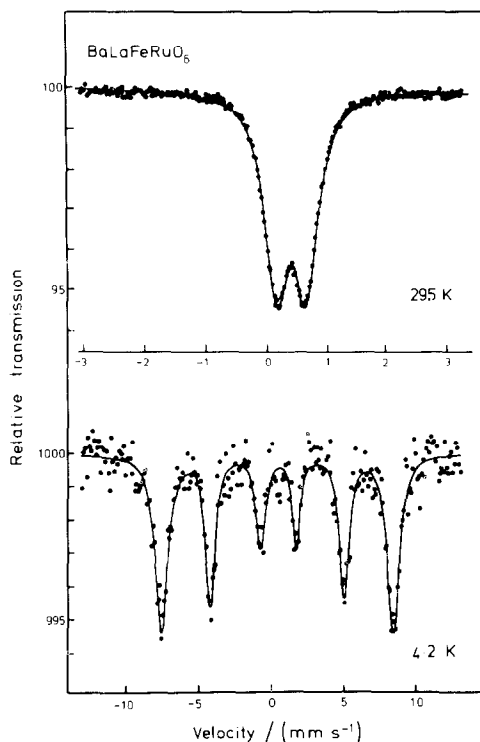
FIG. 3. ^{57}Fe Mössbauer spectra at 295 and 4.2 K for BaLaFeRuO₆. The computed values of the baseline are 2.19×10^6 and 3.50×10^6, respectively.

broad, consistent with cystallographic disorder both at the A- and the B-sites, which is probably also the cause of the quadrupole splitting. At 4.2 K the spectrum is magnetically split, with a flux density of 49.6 ± 0.2 T

which is also characteristic of high-spin Fe^{III}. Again the linewidths are very broad, ranging from 0.57 mm sec^{-1} for the inner lines to 1.09 mm sec^{-1} for the outer lines.

The ^{99}Ru Mössbauer spectra for the compounds La₂MRuO₆ (M = Mg, Co, Ni, or Zn) all consist of two overlapping lines of approximately equal intensity, with no evidence for magnetic interactions at 4.2 K. The spectrum for the cobalt compound, which shows the greatest separation between the two lines, is shown in Fig. 4 and can in principle be interpreted either as two singlets or as a quadrupole splitting. To resolve the problem we have curve-fitted the spectrum in various ways. The line positions, −0.143 and −0.436 mm sec^{-1}, resulting from a two-peak fit would represent rather unusual chemical isomer shifts for ruthenium in oxide phases and on this basis alone this model seems unlikely to be correct. Moreover, the spectrum can be fitted very satisfactorily as a six-line quadrupole-split pattern with a computed value for the chemical isomer shift of −0.286 mm sec^{-1}, which is typical for Ru^{IV}. In this analysis the only variables were the quadrupole coupling constant e^2qQ_e, the chemical isomer shift δ, the linewidth Γ, a single value to scale the intensities, and the baseline; the ratio of the quadrupole moments was fixed to the value $Q_e/Q_g = +2.94$ (15) and the E2/M1 mixing ratio at

TABLE III
^{57}Fe Mössbauer Parameters for BaLaFeRuO₆

Temperature, T (K)	Chemical isomer shift, δ^a (mm sec^{-1})	Quadrupole splitting, $\frac{1}{2}e^2qQ$ (mm sec^{-1})	Magnetic flux density, B (T)	Linewidth, Γ (mm sec^{-1})	$\chi^2(d)^b$
4.2	$+0.50 \pm 0.01^c$	$\varepsilon \sim 0^d$	49.6 ± 0.2	0.57–1.09	192 (227)
100.0 ± 0.2	$+0.51 \pm 0.01$	0.49 ± 0.01	0	0.50, 0.47	249 (239)
295 ± 5	$+0.40 \pm 0.01$	0.49 ± 0.01	0	0.47, 0.46	402 (239)

^{a} Relative to metallic iron.

^{b} d = Degrees of freedom.

^{c} This spectrum was recorded with the source at 4.2 K, but the shift has been corrected to refer to a room temperature source.

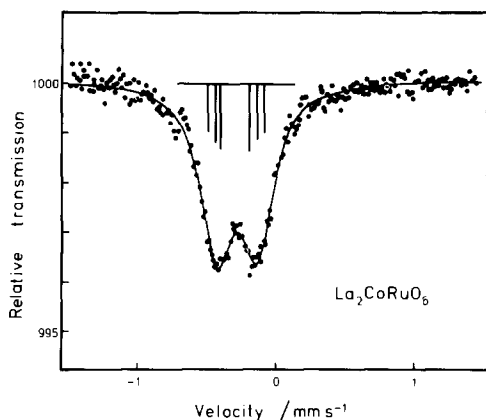^{d} $\varepsilon = (e^2qQ/8)(1-3\cos^2\theta)$.

FIG. 4. ^{99}Ru Mössbauer spectrum at 4.2 K for La$_2$CoRuO$_6$. The computed value of the baseline is 29.9×10^6.

quadrupole splitting in the Ru^{IV} resonance is not unexpected despite the overall cubic symmetry of the unit cell and arises from the non-cubic local environment at the individual ruthenium sites.

General Discussion

The ordered perovskite structure $M^{II}M^{III}BB'O_6$ adopted by the compounds BaLaMRuO$_6$ is a face-centered cubic structure with the space group $Fm3m$, in which the B and B' cations form a NaCl-type lattice with both cations in perfect octahedral coordination. Each oxygen is coordinated to 1 B cation, 1 B' cation, and 4 A-site cations M^{II} or M^{III}, whereas each A-site cation is coordinated to 12 oxygens.

When B is a paramagnetic cation and B' is diamagnetic, the dominant magnetic interaction is a superexchange involving the diamagnetic intermediary O–B'–O, rather than a direct metal–metal interaction (16). For a given oxidation state the 180° B–O–B'–O–B interaction is an order of magnitude weaker than the B–O–B interaction found in normal perovskites, though the B–B distances differ by only a factor of 2. It is,

the value $\delta^2 = 2.72$ (12). From the analysis it was not possible to determine the sign of the quadrupole coupling constant e^2qQ_c, because equally good fits were obtained regardless of whether the sign was taken as positive (as in Fig. 4) or negative. The quadrupole splittings for the other compounds were smaller than that for the cobalt compound and have not been analyzed in detail. The appearance of

TABLE IV

^{99}Ru Mössbauer Parameters at 4.2 K for the Perovskites La$_2M$RuO$_6$

Phase	Chemical isomer shift, δ^a (mm sec^{-1})	Quadrupole splitting, e^2qQ_e (mm sec^{-1})	Linewidth, Γ (mm sec^{-1})	$\chi^2(d)^b$
La$_2$MgRuO$_6$ ^{c}	-0.24	0.58	0.25, 0.29^d	255 (232)
La$_2$CoRuO$_6$ ^{e}	-0.287 ± 0.002	$+0.617 \pm 0.002$	0.26 ± 0.01^f	204 (242)
	-0.286 ± 0.002	-0.617 ± 0.002	0.26 ± 0.01^f	203 (242)
La$_2$NiRuO$_6$ ^{c}	-0.30	0.44	0.56, 0.44^d	259 (232)
La$_2$ZnRuO$_6$ ^{c}	-0.32	0.54	0.26, 0.48^d	148 (232)

^{a} Relative to ruthenium metal.

^{b} d = Degrees of freedom.

^{c} Fitted with two Lorentzian lines only. Errors associated with the various parameters are ca. ± 0.02 mm sec^{-1}.

^{d} Curve-fitted linewidths of the two Lorentzians.

^{e} Fitted with the full six-line quadrupole pattern.

^{f} Linewidth of each of the six components.

therefore, perhaps surprising that the compounds BaLaMRuO$_6$ (M = Mg or Zn) show long-range order, particularly as LaRuO$_3$ itself is paramagnetic at 4.2 K (14). The same comment applies to the related compounds Ca$_2$$LnRuO_6$ (Ln = Y or La) which we have shown recently to be antiferromagnetic, despite the fact that CaRuO$_3$ is paramagnetic down to 4.2 K (7). The crucial factor in both systems is undoubtedly the greater strength of the exchange interactions between Ru^V ions compared with those in the cases of Ru^{III} and Ru^{IV}.

Perhaps equally notable is the observation that the Néel points for the compounds BaLaMRuO$_6$ (M = Mg or Zn) are comparable with those for the analogous compounds containing the paramagnetic Co^{II} and Ni^{II} ions (Fig. 1). Intuitively, much stronger superexchange interactions might have been expected for the latter. Instead, there appears to be an approximately regular increase in T_N with decreasing ionic radius of the divalent metal cation, and therefore with decreasing cell parameter (see Table I). The increase in the overlap integrals with decreasing distance is therefore an important factor influencing the relative strengths of the superexchange interactions in this series. However, the possibility that the observed correlation might arise from the fortuitous cancellation of several other effects cannot be ruled out. In this respect it is interesting to note that the opposite behavior is observed in a series of cubic, ordered perovskites of Ni, for which the Néel temperature has been found to increase with increasing radius of the B cation (17). In another study a correlation has been observed between the Néel temperature and the ionization potential of the diamagnetic B cation (16). Clearly the strength of the exchange interactions is controlled by the interplay of several factors and each system has to be considered individually.

The observation of antiferromagnetism rather than ferromagnetism in the

compounds BaLaMRuO$_6$ (M = Mg or Zn) is consistent with Goodenough's predictions of a weak antiferromagnetic superexchange interaction between d^3 ions. This follows because the signs of the B-O-B'-O-B and B-O-B superexchange interactions are predicted to be the same (18). By contrast, the behavior of the analogous Fe, Co, and Ni compounds is more difficult to rationalize. In these compounds the 180° superexchange interactions of the type Ru^V-O-M^{II} (M = Co or Ni) or Ru^{IV}-O-Fe^{III} should all be ferromagnetic according to Goodenough's rules, but this does not appear to be the case at low temperatures, where the plots of $1/\chi'_M$ vs T show distinct minima, indicative of antiferromagnetism. In view of the fact that the Ru-O-M-O-Ru antiferromagnetic superexchange leads to Néel temperatures of ca. 20 K in the Mg and Zn compounds, it is not unreasonable to expect this interaction to become important in the Fe, Co, and Ni compounds at these temperatures. However, it is not clear why it appears to dominate the (predicted) ferromagnetic Ru^V-O-M^{II} (M = Co or Ni) and Ru^{IV}-O-Fe^{III} interactions. It is perhaps significant that both BaLaCoRuO$_6$ and BaLaNiRuO$_6$ appear to give positive extrapolated θ values, indicative of ferromagnetic interactions, despite the clear minima in $1/\chi$ vs T at low temperatures. These results are not well understood at present and further work is planned to resolve the problem (5).

Turning finally to the compounds La$_2$$MRuO_6$, we note that none of these is magnetically ordered at 4.2 K. This is consistent with the weaker superexchange interactions associated with Ru^{IV} compared with Ru^V, coupled with the presence of La^{III} as the only ions on the A-sites. The greater electron-pair acceptor strength (Lewis acidity) of La^{III} compared to Ba^{II} results in a more effective competition with ruthenium for the oxygen anion orbitals involved in the superexchange interaction, and precludes long-range magnetic order.

Acknowledgments

References

1. P. C. DONOHUE, L. KATZ, AND R. WARD, Inorg. Chem. 5, 339 (1966).

2. T. C. GIBB, R. GREATREX, N. N. GREENWOOD, AND K. G. SNOWDON, J. Solid State Chem. 14, 193 (1975).

3. N. N. GREENWOOD, F. M. DA COSTA, AND R. GREATREX, Rev. Chim. Minérale 13, 133 (1976).

4. T. C. GIBB, R. GREATREX, AND N. N. GREENWOOD, J. Solid State Chem. 31, 153 (1980).

5. J. DARRIET AND P. HAGENMULLER, private communication.

6. P. C. DONOHUE AND E. L. McCANN, Mater. Res. Bull. 12, 519 (1977).

7. R. GREATREX, N. N. GREENWOOD, M. LAL, AND I. FERNANDEZ, J. Solid State Chem. 30, 137 (1979).

8. F. GALASSO AND W. DARBY, Inorg. Chem. 4, 71 (1965).

9. R. C. BYRNE AND C. W. MOELLER, J. Solid State Chem. 2, 228 (1970).

10. W. KLEMM AND E. WEISE, Z. Anorg. Allg. Chem. 279, 74 (1955).

11. G. BLASSE, Philips Res. Rep. 20, 327 (1965).

12. T. C. GIBB, R. GREATREX, N. N. GREENWOOD, AND P. KASPI, J. Chem. Soc. Dalton Trans., 1253 (1973).

13. T. C. GIBB, R. GREATREX, N. N. GREENWOOD, D. C. PUXLEY, AND K. G. SNOWDON, J. Solid State Chem. 11, 17 (1974).

14. F. M. DA COSTA, R. GREATREX, AND N. N. GREENWOOD, J. Solid State Chem. 20, 381 (1977).

15. F. M. DA COSTA, T. C. GIBB, R. GREATREX, AND N. N. GREENWOOD, Chem. Phys. Lett. 36, 655 (1975).

16. G. BLASSE, Proc. Int. Conf. Magn. Nottingham, 350 (1964).

17. J. PORTIER, C.R. Acad. Sci. Paris Ser. C 286, 687 (1978).

18. J. B. GOODENOUGH, "Magnetism and the Chemical Bond," p. 174, Interscience, New York (1963).