Ruthenium-99 Mössbauer Studies of the Magnetic Properties of Ternary and Quaternary Ruthenium(IV) Oxides

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Ruthenium-99 Mössbauer spectra have been obtained for the ternary oxides $SrRuO_3$, $CaRuO_3$, $BaRuO_3$, and $Y_2Ru_2O_7$ and for the quaternary oxides $Sr(Ru_{1-x}Ir_x)O_3$ ($x = 0{\cdot}1$ and $0{\cdot}2$) and $Sr(Ru_{0\cdot7}Mn_{0\cdot3})O_3$. The spectrum of $SrRuO_3$ reveals the first example of a hyperfine magnetic field in a ruthenium compound; the internal field of 352 kG at 4·2 K is compatible with the ferromagnetic moment derived from neutron-diffraction data, and confirms the collective-electron magnetism model for this perovskite. A more precise value for the $E2/M1$ mixing ratio of $2{\cdot}72 \pm 0{\cdot}17$ has been obtained for the ^{99}Ru Mössbauer γ transition. The oxide $CaRuO_3$ shows only a single line and hence no magnetic ordering even at 4·2 K; it is not antiferromagnetic as previously reported but is Curie–Weiss paramagnetic. The oxide $BaRuO_3$ also gives a singlet; there is no long-range antiferromagnetic ordering, but within each cluster of three face-sharing RuO_6 units localised pairing of the $4d$ electrons takes place. The oxide $Y_2Ru_2O_7$ is magnetically ordered at 4·2 K, with a hyperfine field of 126 kG. Substitution of ruthenium by iridium in the oxide $SrRuO_3$ reduces the field at ruthenium by approximately 60 kG for each iridium nearest neighbour, whereas in the case of manganese substitution the reduction for each manganese neighbour is only 22 kG.

THE Mössbauer effect in ruthenium-99 is being increasingly applied to the study of chemical problems, and in the past two years ten papers on the subject have appeared.[1-10] These have dealt mainly with the spectra of co-ordination complexes of ruthenium and, apart from the preliminary communication of our own work on the oxide $SrRuO_3$,[10] there have been no other reports of applications in the field of solid-state chemistry. The latter study suggested that ^{99}Ru Mössbauer spectroscopy might provide the basis for a detailed investigation of related ternary and quaternary ruthenium oxides and so lead to an understanding of the magnetic properties of the $4d$ transition series. We have therefore undertaken a systematic study of such materials. The present paper reports measurements on the ternary oxides $SrRuO_3$, $CaRuO_3$, $BaRuO_3$, and $Y_2Ru_2O_7$ and on the quaternary oxides $Sr(Ru_{1-x}Ir_x)O_3$ ($x = 0{\cdot}1$ and $0{\cdot}2$) and $Sr(Ru_{1-x}Mn_x)O_3$ ($x = 0{\cdot}3$), all of which contain ruthenium in oxidation state IV.

The oxide $SrRuO_3$ is ferromagnetic (T_C 160 K)[11] with a perovskite structure which is close to cubic.[12] Its Mössbauer spectrum reveals the first example of a hyperfine magnetic field in a ruthenium compound. The only other reported observation of a resolved magnetic hyperfine splitting of the ^{99}Ru resonance has been for an alloy of ruthenium (2·3 atom%) in metallic iron.[13] Other related work on the measurement of hyperfine fields has concerned ^{99}Ru perturbed angular-correlation studies in iron and nickel,[14] and ^{101}Ru spin-echo n.m.r. studies in iron, cobalt, and nickel;[15] in all cases the ruthenium was an impurity in a magnetically concentrated metal. The internal field in the oxide $SrRuO_3$ of 352 kG (= 35·2 T) at 4·2 K is shown to be compatible with the ferromagnetic moment derived from neutron-diffraction data,[16] and is consistent with the collective-electron magnetism model for this compound.

The oxide $CaRuO_3$ also has the perovskite structure but is more distorted[12] and, although it has been described as being antiferromagnetic[11,16] with a Néel temperature of 110 ± 10 K,[16] the Mössbauer results show conclusively that the material is, in fact, not

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[1] G. Kaindl, W. Potzel, F. Wagner, U. Zahn, and R. L. Mössbauer, *Z. Physik*, 1969, **226**, 103.

[2] C. A. Clausen, R. A. Prados, and M. L. Good, *Chem. Comm.*, 1969, 1188.

[3] C. A. Clausen, R. A. Prados, and M. L. Good, *J. Amer. Chem. Soc.*, 1970, **92**, 7484.

[4] W. Potzel, F. E. Wagner, U. Zahn, R. L. Mössbauer, and J. Danon, *Z. Physik*, 1970, **240**, 306.

[5] W. Potzel, F. E. Wagner, R. L. Mössbauer, G. Kaindl, and H. E. Seltzer, *Z. Physik*, 1971, **241**, 179.

[6] C. A. Clausen, R. A. Prados, and M. L. Good, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 485.

[7] C. A. Clausen, R. A. Prados, and M. L. Good, *Chem. Phys. Letters*, 1971, **8**, 565.

[8] C. A. Clausen, R. A. Prados, and M. L. Good, 'Mössbauer Effect Methodology,' ed. I. J. Gruverman, Plenum Press, 1971, vol. 6, p. 31.

[9] R. Greatrex, N. N. Greenwood, and P. Kaspi, *J. Chem. Soc.* (*A*), 1971, 1873.

[10] T. C. Gibb R. Greatrex, N. N. Greenwood, and P. Kaspi, *Chem. Comm.*, 1971, 319.

[11] A. Callaghan, C. W. Moeller, and R. Ward, *Inorg. Chem.*, 1966, **5**, 1572.

[12] J. J. Randall and R. Ward, *Inorg. Chem.*, 1959, **81**, 2629.

[13] O. C. Kistner, *Phys. Rev.*, 1966, **44**, 1022.

[14] D. A. Shirley, S. S. Rosenblum, and E. Matthias, *Phys. Rev.*, 1968, **170**, 363.

[15] M. Kontani and J. Itoh, *J. Phys. Soc. Japan* 1967, **22**, 345.

[16] J. M. Longo, P. M. Raccah and J. B. Goodenough *J. Appl. Phys.*, 1968, **39**, 1327.

magnetically ordered even at 4·2 K. The oxide $BaRuO_3$ has a hexagonal nine-layer structure in which there are strings of three face-sharing octahedra connected by corner sharing of end octahedra.[12,17] It has been described as being antiferromagnetic.[11] The Mössbauer data indicate that it does not display long-range antiferromagnetic ordering, but that there is strong antiparallel coupling of the $4d$ electrons within each cluster of three face-sharing RuO_6 units. The oxide $Y_2Ru_2O_7$ has the pyrochlore structure.[18] Little was known about its magnetic properties prior to the present study, but it is now found to be magnetically ordered at 4·2 K with a hyperfine field of *ca.* 126 kG.

Iridium [12] and manganese both replace ruthenium in the perovskite lattice and the resulting quaternary oxides have been studied in order to elucidate the nature of the exchange forces between ruthenium and the other cations. It appears that each iridium nearest neighbour reduces the field at ruthenium by about 60 kG, whereas the reduction for each manganese nearest neighbour is only about 22 kG. There is therefore little or no magnetic interaction between ruthenium and iridium, but appreciable interaction between ruthenium and manganese ions in this system.

EXPERIMENTAL

The Mössbauer spectra were obtained with both source and absorber at either 77 or 4·2 K using the apparatus described previously.[9] The radioactive source differed from that used in our earlier experiments and was prepared by a ^{99}Ru(d,2n)^{99}Rh reaction on a pellet of natural ruthenium metal, as described by Mössbauer and his coworkers.[1] The linewidth observed, using this source in conjunction with a natural ruthenium metal absorber, was 0·36 mm s^{-1}, rather narrower than that generated by our earlier enriched source. The absorbers consisted typically of *ca.* 1 g cm^{-2} of the powdered oxide.

Preparation and Characterisation of the Oxide Phases.—The mixed oxides were prepared by published methods,[12,17] from stoicheiometric proportions of ruthenium metal and alkaline-earth carbonates; transition metals, or their oxides, were included in the preparation of the substituted ruthenium oxides. The metal oxides and carbonates were high-purity materials (*e.g.* Johnson, Matthey, grade II high-purity chemicals). The reactants were weighed out on an analytical balance, intimately mixed and ground repeatedly in an agate mortar until a homogeneous mixture was obtained, and then fired in platinum crucibles in air at *ca.* 1200 °C (24 h). The mixtures were given three or four intermediate grindings during the reaction period to ensure homogeneity of the products, which were characterised by X-ray diffraction using cobalt K-radiation (λ 179·0 pm). No chemical analyses of the compounds were made.

Calcium ruthenium(IV) *trioxide.* $CaCO_3$ (1·121 g) and Ru (1·123 g) were heated together as described above. A violet-black microcrystalline powder (2·10 g) was obtained. This compound has the perovskite structure and has been indexed with an orthorhombic unit cell, from which lattice constants $a = 553$, $b = 536$, and $c = 767$ pm were derived.[12] The d spacings observed, from an X-ray diffraction pattern of the sample used here, agree with published data and no extraneous lines were present.

Strontium ruthenium(IV) *trioxide.* $SrCO_3$ (1·555 g) and Ru (1·066 g) were heated together, the product being a violet-black powder (2·48 g). This compound has the perovskite structure and has been indexed with an orthorhombic unit cell, with lattice constants $a = 557$, $b = 553$, and $c = 785$ pm.[12]

Barium ruthenium(IV) *trioxide.* $BaCO_3$ (2·018 g) and Ru (1·035 g) yielded a blue-black product (2·92 g). This compound has the hexagonal nine-layer structure and the observed d spacings agree well with those reported by Randall and Ward.[12]

Diyttrium diruthenium(IV) *heptaoxide.* A sample (2·12 g) was prepared by heating together Y_2O_3 (1·021 g) and Ru (0·914 g) as described above. The oxide Y_2O_3 was prepared by thermally decomposing a yttrium ammonium oxalate complex precipitated from yttrium nitrate solution. The oxide $Y_2Ru_2O_7$ has the pyrochlorite structure with $a =$ 101·44 pm, and the observed d spacings were indexed using a cubic unit cell with the published dimensions.[18]

The system $Sr(Ru_{1-x}Ir_x)O_3$. Single-phase products were prepared for $x = 0·1$ (and 0·2) using the following weights of starting materials: $SrCO_3$, 1·623 (1·4757); Ru, 1·000 (0·8070); and Ir, 0·2112 (0·3802 g). X-Ray diffraction patterns were very similar to those of $SrRuO_3$.

The system $Sr(Ru_{1-x}Mn_x)$. Only one sample ($x = 0·3$) was prepared. The proportions of reactants used were: $SrCO_3$ (2·085); Ru (1·000); and MnO_2 (0·3684 g); 3·15 g of product were obtained. The d spacings obtained from the X-ray diffraction pattern of this compound have not yet been indexed. It appears that the structure is considerably distorted from that of $SrRuO_3$, many lines being split compared to equivalent lines for $SrRuO_3$.

RESULTS AND DISCUSSION

Ternary Oxides.—$SrRuO_3$. Strontium ruthenium(IV) trioxide has the perovskite structure in which RuO_6 octahedra share corners so that each oxygen atom is common to two ruthenium atoms.[12] There is some doubt as to whether the phase can be oxygen deficient.[12,13] It orders ferromagnetically below 160 K [11] and shows a collective-electron magnetism and metallic properties [11] which result in characteristic behaviour in the electrical resistivity [19] and the pressure dependence of the Curie temperature.[20] The saturation moment has been estimated as 0·85 B.M. at 77 K from bulk-magnetisation measurements,[11] and 1·4 ± 0·4 B.M. from neutron-diffraction data at 4·2 K,[13] both values being much lower than expected for a $4d^4$ low-spin configuration ($S = 1$) with localised-electron magnetism.

A typical Mössbauer spectrum obtained with both source and absorber (1·27 g cm^{-2} of $SrRuO_3$) at 4·2 K is shown in Figure 1(*a*). The absorption dip is 0·16% with a total of 122×10^6 counts per channel. The transition between the $I_e = 3/2$ excited state and the $I_g = 5/2$ ground state results in 18 magnetic hyperfine

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[17] P. C. Donahue, L. Katz, and R. Ward, *Inorg. Chem.*, 1965, **4**, 306.

[18] F. Bertaut, F. Forrat, and M. C. Montmony, *Compt. rend.*, 1959, **249**, 829.

[19] Y. Noro and S. Miyahara, *J. Phys. Soc. Japan*, 1969, **27**, 518.

[20] M. Menyuk, J. A. Kafalas, K. Dwight, and J. B. Goodenough, *J. Appl. Phys.*, 1969, **40**, 1324.

lines. The relative intensities for a powdered (non-oriented) sample may be calculated directly from Clebsch–Gordan coefficients. Both $E2$ and $M1$ multipolarity terms must be included because the $E2/M1$ mixing ratio, $\boldsymbol{\delta}^2$, is large. In the first instance we adopted Kistner's value for $\boldsymbol{\delta}^2$ of 2·7 ± 0·6, together with his ratio for the nuclear magnetic moments, μ_e/μ_g = 0·455 ± 0·010. These parameters enabled the interdependence of the component lines to be established.

In our preliminary communication of this data, a least-squares fit was made using only five variables: (*a*) the hyperfine magnetic field; (*b*) the chemical-isomer shift relative to ruthenium metal; (*c*) the baseline; (*d*) a single value to scale the relative intensities; and (*e*) the linewidth. The final fit had a value of $\chi^2 = 184$ on 194 degrees of freedom. The fit was not very sensitive to the value of $\boldsymbol{\delta}^2$, but in view of the large uncertainty in the published value of this parameter it seemed advisable to redetermine it for use in later calculations. A second least-squares fit, with $\boldsymbol{\delta}^2$ and μ_e/μ_g as variables, gave an almost identical final fit. The new values of $\boldsymbol{\delta}^2$ = 2·72 ± 0·17 and μ_e/μ_g = 0·456 ± 0·002 are in excellent agreement with Kistner's data but establish more precise values for these parameters. The value of μ_e is −0·284 ± 0·006 μ_N, whence μ_g = −0·623 ± 0·019 μ_N.[21] The latter value led to a value for the magnetic field in $SrRuO_3$ at 4·2 K of 352 kG. The other experimental parameters are given in the Table. The sign of the field was not determined but is assumed to be negative.

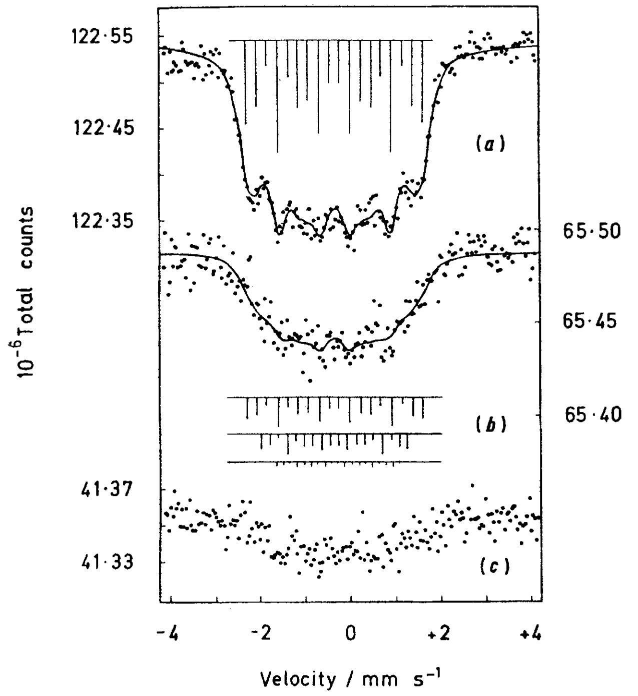

FIGURE 1 Mössbauer spectra at 4·2 K of (*a*) $SrRuO_3$, (*b*) $Sr(Ru_{0\cdot9}Ir_{0\cdot1})O_3$, and (*c*) $Sr(Ru_{0\cdot8}Ir_{0\cdot2})O_3$ relative to a ^{99}Rh–Ru metal source at the same temperature

Recomputation of the Mössbauer data, with an axially symmetric quadrupole splitting of the excited state $\frac{1}{2}e^2qQ_e$ parallel to the magnetic field (neglecting any ground-state splitting because $Q_e/Q_g > 3$), gave a value for $\frac{1}{2}e^2qQ_e$ of −0·010 ± 0·006 mm s^{-1} with $\chi^2 = 181$. We therefore consider the quadrupole splitting to be zero within experimental error. This implies that the slight orthorhombic distortion of the perovskite structure of $SrRuO_3$ has negligible effect on the degeneracy of the ruthenium t_{2g} levels; alternatively any electric-field gradient arising from electronic imbalance is compensated by a q_{lattice} value of opposite sign.

^{99}Ru Mössbauer parameters for some oxide phases *

Compound	T/K	δ/mm s^{-1}	Γ/mm s^{-1}	% absorption	H/kG
$CaRuO_3$	4·2	−0·296(3)	0·40(1)	0·65	0
	77	−0·314(8)	0·34(2)	0·14	0
$SrRuO_3$	4·2	−0·325(7)	0·43(2)	0·16	352(15)
	77	−0·305(21)	0·35(5)	0·10	315(15)
$BaRuO_3$	4·2	−0·257(5)	0·40(2)	0·31	0
	77	−0·253(16)	0·46(6)	0·10	0
$Y_2Ru_2O_7$	4·2	−0·226(19)	(0·43) †	0·14	126(8)
$Sr(Ru_{0\cdot9}Ir_{0\cdot1})O_3$	4·2	−0·318(25)	0·39		352 − 60*n*
$Sr(Ru_{0\cdot7}Mn_{0\cdot3})O_3$	4·2	−0·16(5)	(0·43) †		352 − 22*n*

* δ is the chemical-isomer shift and should not be confused with the $E2/M1$ mixing ratio $\boldsymbol{\delta}^2$. Its magnitude is quoted relative to the ^{99}Rh–Ru metal source at the same temperature as the absorber. † Parameter fixed at stated value.

Few data are available for magnetic hyperfine fields in the 4*d* transition series. Calculations have shown that the Fermi core-polarisation term for a single unpaired 4*d*-electron should be *ca.* −370 kG.[14] On this basis the observed field at 4·2 K corresponds to 1·0 unpaired electron on the ruthenium atom, a value which compares favourably with the magnetic-susceptibility and neutron-diffraction data mentioned earlier. It is difficult to assess the role of any orbital contribution to the hyperfine field, because the degree of anisotropy (if any) at the ruthenium atom is not known. However, assuming that this is small, our data are fully consistent with the reduced ferromagnetic moment of this compound.

$CaRuO_3$.—Calcium ruthenium(IV) trioxide also has the perovskite structure but the orthorhombic distortion is much greater than that for the strontium analogue. Callaghan *et al.*[11] found that the compound had a negative Weiss temperature and followed a Curie–Weiss law at high temperatures. Measurements were made only down to 77 K and, although the authors did not find a minimum in their plot of reciprocal bulk-molar magnetic susceptibility against temperature, there was a deviation from linearity at low temperatures which they suggested might be due to some short-range order above an antiferromagnetic temperature T_N.[11] Longo *et al.*[16] repeated the susceptibility measurements on the compound in fields of <17 kG and extended them to temperatures as low as 4·2 K. Although there was no

[21] E. Matthias, S. S. Rosenblum, and D. A. Shirley, *Phys. Rev.* (*B*), 1965, **139**, 532.

minimum in the reciprocal susceptibility against temperature plot, as postulated by Callaghan, there was a small inflexion at *ca.* 110 K. Furthermore, on the basis of a plot of magnetisation against applied field, they postulated a small parasitic ferromagnetism equal to $(3{\cdot}2 \pm 0{\cdot}4) \times 10^{-2}$ e.m.u. g^{-1} at 4·2 K. It was therefore concluded that the compound was antiferromagnetic, probably of the collective-electron type (from its conductivity), with a small parasitic ferromagnetism that eliminated a well defined minimum at the Néel temperature, $T_N = 110$ K.

In the present work, Mössbauer spectra were recorded at 77 and 4·2 K on a powdered sample of thickness 1·05 g cm^{-2}. As can be seen from Figure 2(*a*), a narrow single line was observed, even at 4·2 K, showing that long-range magnetic order was absent. It is also of interest that no identifiable magnetic peaks were observed by neutron diffraction.[22] An unpowdered, crystalline sample gave similar Mössbauer results, so that superparamagnetism is ruled out. The observed parameters are given in the Table.

In view of the conflict between the present results and those of Longo *et al.*, we decided to repeat the measurement of the magnetic susceptibility down to 4·2 K, using a low-temperature translation balance. An essentially smooth curve was obtained with no sign of any inflexion in the proposed magnetic-transition region. At this point it can be mentioned that, although it is a good conductor, the oxide $CaRuO_3$ is less conducting than is $SrRuO_3$.[11] It seems, therefore, that the sample is essentially Langevin paramagnetic, with a capacity to conduct electricity in a way as yet undetermined.*

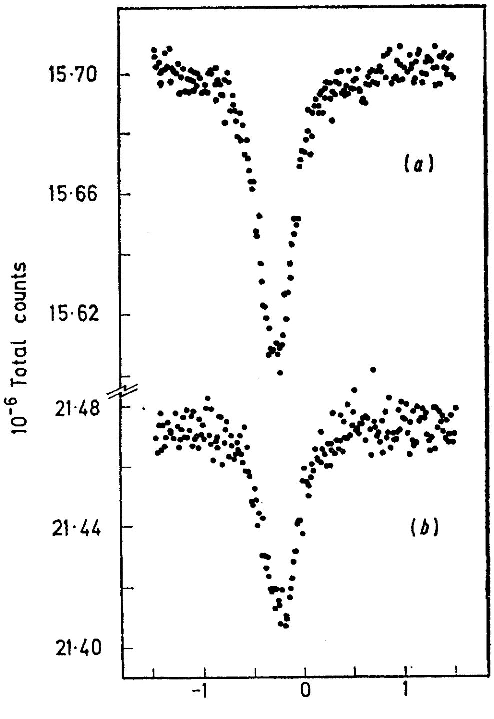

FIGURE 2 Mössbauer spectra at 4·2 K of (*a*) $CaRuO_3$ and (*b*) $BaRuO_3$ relative to a ^{99}Rh–Ru metal source at the same temperature

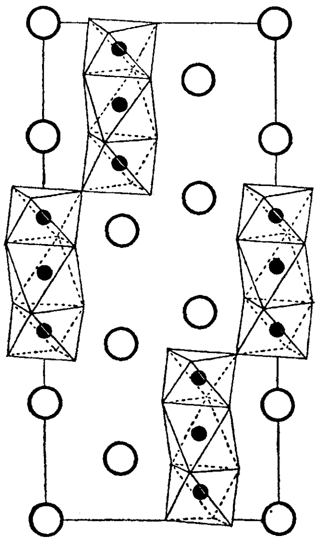

FIGURE 3 Schematic representation of the structure of $BaRuO_3$ showing the inter-relation of the RuO_6 octahedra

$BaRuO_3$. Barium ruthenium(IV) trioxide has the nine-layer hexagonal structure[17] (Figure 3), in which there are strings of face-sharing RuO_6 octahedra along the *c*-axis connected by corner sharing of the end octahedra. The overall magnetic susceptibility of the compound is low and rises with temperature to a broad maximum at about 430 K, after which it falls off more slowly. The compound has been described as antiferromagnetic and has a high electrical conductivity both at 77 K and room temperature.[11]

The Mössbauer spectrum of this material showed only a single, narrow line at temperatures of 77 and 4·2 K [Figure 2(*b*)]. The two non-equivalent ruthenium environments present in the nine-layer structure are therefore not distinguished in the Mössbauer spectrum, but the observations indicate conclusively that there is no long-range magnetic order in the compound. The Mössbauer parameters are given in the Table.

To understand the magnetic properties of $BaRuO_3$, it is helpful to consider first the compound $Ba_3Ru_2MgO_9$, which contains isolated pairs of face-sharing RuO_6 octahedra separated by MgO_6 octahedra, with which they corner-share oxygen. To explain its magnetic behaviour, Callaghan *et al.*[11] compared the observed plot of reciprocal susceptibility against temperature with that based on a theoretical model for two interacting metal atoms, and found sufficient agreement to conclude

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* *Note added in proof:* After submission of our manuscript a paper describing the electronic properties of $CaRuO_3$ and $SrRuO_3$ single crystals came to our attention (R. J. Bouchard and J. Gillson, *Mater. Res. Bull.*, 1972, **7**, 873). The discontinuity in the temperature dependence of electrical conductivity at T_C for $SrRuO_3$ was confirmed, but no discontinuity was observed at the reported T_N for $CaRuO_3$, consistent with our findings.

[22] J. B. Goodenough, *Progr. Solid-State Chem.*, 1971, **5**, 330.

that there was strong metal–metal interaction between the pairs of ruthenium atoms. The oxide $BaRuO_3$ also has clusters of face-sharing octahedra, but is a more complex system, and our attempts at a mathematical description were unsuccessful. In the linear clusters of three atoms there are two metal–oxygen–metal interactions. The magnetic susceptibility data indicate that the metal–metal interactions are considerably stronger than the metal–oxygen–metal interactions, and dominate the magnetic properties.[11] This conclusion is reflected in the electrical conductivity of the compound, which, although high, is not metallic.

The discussion is clarified by referring to a possible molecular-orbital energy-level diagram for the 4*d* electrons of the cluster of three ruthenium atoms (Figure 4). It can be seen that the ground state of the cluster is diamagnetic. This behaviour is sometimes called (rather misleadingly) short-range antiferromagnetism. The susceptibility will therefore be anomalously low at low temperature, as observed, and its temperature dependence will be governed by the thermal population of paramagnetic higher states as the temperature is raised, with a high-temperature limit of $S = 3$ from six unpaired electrons. In many respects the behaviour is similar to the low susceptibilities of iron(III) compounds such as $[Fe(salen)]_2O$ [salen = *NN'*-ethylenebis(salicylaldiminato)] where the Mössbauer spectrum howss no hyperfine splitting and there is a strong localised coupling of the $S = 5/2$ spins.[23]

$Y_2Ru_2O_7$. Diyttrium diruthenium(IV) heptaoxide has the pyrochlore structure, in which there are zig-zag rows of corner-shared RuO_6 octahedra making cation–anion–cation angles of *ca.* 135 °C. Goodenough has pointed out that this arrangement may allow somewhat larger interactions of *d* orbitals for giving π-bands than in the perovskite structure.[22]

The Mössbauer spectrum of a sample of $Y_2Ru_2O_7$ of thickness 1·19 g cm^{-2} recorded at 4·2 K is shown in Figure 5(*b*). A single quadrupole spectrum of this span (*ca.* 0·8 mm s^{-1}) would be well resolved and it is unlikely that there are a number of overlapping quadrupole spectra to give a smooth band. It can therefore be assumed that $Y_2Ru_2O_7$ is magnetically ordered. The spectrum was computed in a similar manner to the $SrRuO_3$ spectrum, with the linewidth fixed at 0·43 mm s^{-1} to prevent an unrealistic calculation. The computed line fit is included in Figure 5. The magnetic hyperfine field is 126 ± 8 kG.

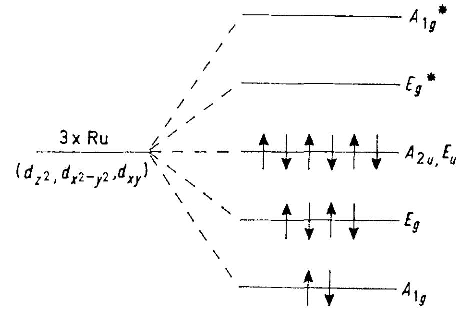

FIGURE 4 Possible molecular-orbital scheme (not to scale) for the 4*d* electrons in the cluster of three ruthenium atoms in $BaRuO_3$

There are no magnetic susceptibility data at present to substantiate these findings or to indicate the type of magnetic ordering. Likewise there are no conductivity data to indicate whether the magnetism is of the collective-electron or localised-electron type. All members of the lanthanide series form $Ln_2Ru_2O_7$ type compounds of the pyrochlore structure and, like $Y_2Ru_2O_7$, their magnetic properties have yet to be investigated.

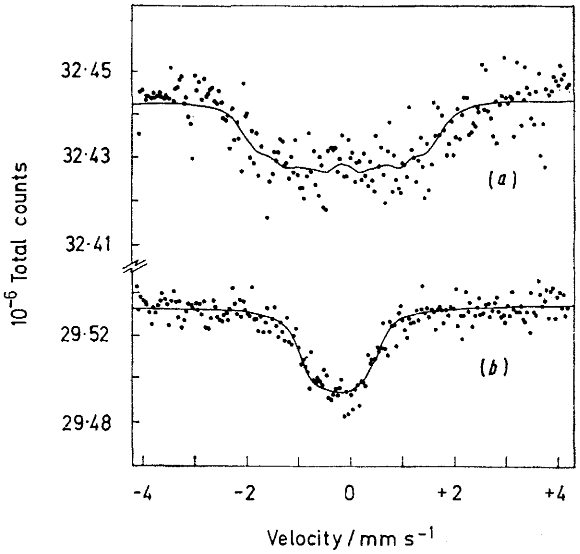

FIGURE 5 Mössbauer spectra at 4·2 K of (*a*) $Sr(Ru_{0\cdot7}Mn_{0\cdot3})O_3$ and (*b*) $Y_2Ru_2O_7$ relative to a ^{99}Rh–Ru metal source at the same temperature

Quaternary Oxides.—From the results already discussed it is clear that ^{99}Ru Mössbauer spectroscopy provides a very powerful method for studying the magnetic state of ruthenium in oxide materials. In the following sections we investigate the potential use of the technique in elucidating exchange forces between ruthenium and other cations in substituted compounds of the type $Sr(Ru_{1-x}M_x)O_3$.

The System $Sr(Ru_{1-x}Ir_x)O_3$. Iridium will substitute for ruthenium up to $x = 0{\cdot}5$,[12] and lattice constants of samples of $Sr(Ru_{1-x}Ir_x)O_3$ are exactly the same as those for $SrRuO_3$. The compounds also retain their metallic properties. The samples examined were found to be ferromagnetic by bulk-susceptibility measurements, with Curie temperatures similar to that of $SrRuO_3$ (155 K for the $x = 0{\cdot}1$ compound).

Mössbauer spectra were recorded for samples where $x = 0{\cdot}1$ and 0·2. The former gave a satisfactory spectrum (Figure 1) but for the $x = 0{\cdot}2$ compound the percentage absorption was very weak. For this reason samples with even higher values of x were not studied.

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[23] W. M. Reiff, W. A. Baker, and N. E. Erickson, *J. Amer. Chem. Soc.*, 1968, **90**, 4794.

It can be seen that the extremities of the $x = 0{\cdot}1$ spectrum are more rounded than those of the $SrRuO_3$ spectrum. This is thought to be caused by the presence of a number of overlapping components from ruthenium atoms in different environments experiencing different magnetic fields. An attempt was made to compute the spectra, with the assumption that the magnetic field at a ruthenium ion decreases proportionally with the number of iridium nearest neighbours, the effects of more distant ruthenium and iridium ions being neglected. The field at a ruthenium site having only ruthenium ions as nearest neighbours was therefore assumed to be the same as that in $SrRuO_3$, and the maximum field was fixed as such in the computation. The reduction in field due to the presence of each iridium nearest neighbour to ruthenium was then found. In the perovskite structure each cation has six nearest cation neighbours in an octahedral array and the ruthenium atom may, therefore, be surrounded by between zero and six iridium neighbours in place of ruthenium. It was assumed that the substitution was completely random, which leads to a binomial distribution of probabilities that a ruthenium cation is surrounded by a certain number of iridium cations. The resulting probabilities $W(n)$ of there being n nearest iridium neighbours to a ruthenium cation, at various concentrations, x, of iridium are as follows.

		$x = 0{\cdot}1$	$x = 0{\cdot}2$	$x = 0{\cdot}3$
$W(0)$	=	0·531	0·262	0·117
$W(1)$	=	0·354	0·393	0·300
$W(2)$	=	0·098	0·246	0·324
$W(3)$	=	0·014	0·082	0·185
$W(4)$	=	0·004	0·015	0·059
$W(5)$	=	0·000	0·001	0·010
$W(6)$	=	0·000	0·000	0·000

These probabilities give the relative intensities of the hyperfine components for different numbers of next-nearest iridium neighbours to ruthenium. For each nearest-neighbour Ir to Ru it is assumed that the maximum field H will decrease by a constant amount ΔH, so that for no nearest iridium neighbours the total field is H, for one iridium atom it is $H - \Delta H$, for two iridium atoms it is $H - 2\Delta H$, *etc.* Such behaviour has been recorded, for instance, in the Fe–Si alloys, where in Fe_3Si the value of ΔH is 14% for each Si nearest neighbour.[24]

The spectrum of $Sr(Ru_{0{\cdot}9}Ir_{0{\cdot}1})O_3$ was computed as four hyperfine fields, since for $x = 0{\cdot}1$, the intensities of the spectra for more than three nearest iridium neighbours are very low. The computation gave a chemical-isomer shift of $-0{\cdot}318(25)$ mm s^{-1}, a linewidth of 0·39(5) mm s^{-1}, and $\Delta H = +60(8)$ kG per Ir nearest neighbour; $\chi^2 = 167$ on 194 degrees of freedom. The three most-intense components of the spectrum are illustrated as stick diagrams in Figure 1.

No. of Ir	0	1	2	3
Field/kG	352	$352 - \Delta H$	$352 - 2\Delta H$	$352 - 3\Delta H$
Intensity	0·531	0·354	0·098	0·014

On this analysis of the data, each iridium nearest neighbour reduces the field at ruthenium by 60 kG. The total field around a ruthenium atom is 352 kG in the absence of iridium nearest neighbours. It therefore appears that iridium does not participate, or else participates to only a small degree, in the ruthenium ferromagnetic band; *i.e.* there is little or no interaction between ruthenium(IV) and iridium(IV).

$Sr(Ru_{0{\cdot}7}Mn_{0{\cdot}3})O_3$. The fact that manganese forms Mn^{IV} readily in oxide systems, coupled with the similarity in ionic radius of Mn^{4+} (54 pm) and Ru^{4+} (58 pm), suggested that it might be possible to substitute Mn^{4+} for Ru^{4+} in $SrRuO_3$. A single-phase material of the composition $Sr(Ru_{0{\cdot}7}Mn_{0{\cdot}3})O_3$ was obtained, which had a highly distorted perovskite structure.

The Mössbauer spectrum [Figure 5(*a*)] was collected at 4·2 K and computed in a similar way to that of the iridium compound, but with the linewidth constrained at 0·43 mm s^{-1}. The probabilities, $W(n)$, for a ruthenium atom to be surrounded by n manganese neighbours for 30% Mn substituted randomly into $SrRuO_3$ are tabulated above. The value obtained for ΔH in this case was 22(6) kG and the centroid was at $-0{\cdot}16(5)$ mm s^{-1}. The chi-squared value for the fit was 177 on 195 degrees of freedom. This system therefore contrasts with the preceding one in that there is appreciable interaction between the ruthenium and manganese ions, which leads to a smaller reduction of the maximum field in $Sr(Ru_{0{\cdot}7}Mn_{0{\cdot}3})O_3$ compared to that in $Sr(Ru_{1-x}Ir_x)O_3$. It must be noted, however, that there are structural differences between the two compounds.

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