JOURNAL OF SOLID STATE CHEMISTRY **34**, 121–128 (1980)

^{99}Ru Mössbauer Spectra of Quaternary Ruthenium(V) Oxides with the Hexagonal Barium Titanate Structure

INMACULADA FERNANDEZ, ROBERT GREATREX, AND
NORMAN N. GREENWOOD

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

Received February 15, 1979; in revised form August 13, 1979

^{99}Ru Mössbauer spectra have been recorded at 4.2 K for the quaternary oxides $Ba_3Ru_2MO_9$ (M = Mg, Ca, Sr; Co, Ni, Cu, Zn; and Cd), all of which crystallize with the hexagonal barium titanate structure. The Ca, Sr, and Cd compounds give sharp symmetrical singlets with chemical isomer shifts typical of ruthenium in the +5 oxidation state. The absence of magnetic hyperfine splitting is consistent with the published interpretation of magnetic susceptibility data in terms of binuclear intracluster spin pairing which leads to an $S = 0$ ground state. In contrast, magnetic hyperfine splitting *is* seen for the Mg, Zn, Co, Ni, and Cu compounds; this can be interpreted only in terms of long-range magnetic order and the absence of such an $S = 0$ ground state at 4.2 K. This differs from the published interpretation of the magnetic susceptibility data for $Ba_3Ru_2MgO_9$ in the low-temperature region. The magnetic flux densities at the ruthenium nuclei in the magnetically ordered compounds (32.5–51.6 T) are lower than those normally associated with ruthenium(V), and the spectra cannot be curve fitted satisfactorily with single hyperfine patterns having the natural linewidth. Possible reasons for these observations are discussed.

Introduction

In continuation of our studies on ruthenium-containing oxide phases ((*1*), and references therein) we now report ^{99}Ru Mössbauer spectra at 4.2 K for a series of compounds of general formula $Ba_3Ru_2MO_9$, which crystallize with the ordered hexagonal barium titanate structure (*2*). This structure features pairs of face-sharing RuO_6 octahedra connected through corner sharing with MO_6 octahedra as shown in Fig. 1, and is one of the few which offer the possibility of observing the magnetic behavior of clusters of ruthenium ions isolated from one another in a three-dimensional lattice. However, the structures does not rule out the possibility of cooperative one-dimensional magnetic interactions along the chains, or three-dimensional interactions between the chains. The ruthenium in these compounds was considered to be pentavalent though there was some doubt whether small amounts of ruthenium(IV) might be present in association with oxygen deficiencies (*3*). Magnetic susceptibility measurements have been reported by Callaghan *et al.* (*4*) for $Ba_3Ru_2MgO_9$ and by Darriet *et al.* (*5*) for the Mg, Ca, Sr, and Cd compounds. The results have been interpreted in terms of a model involving spin-coupled binuclear clusters with $S = 0$ ground states, though deviations from the expected behavior were observed below 60 K. These were most pronounced in the case of the Mg compound and were attributed (*5*) to the presence of small numbers of isolated ruthenium ions resulting from partial disorder in the system. Magnetic

0022-4596/80/100121-08$02.00/0

Printed in Great Britain

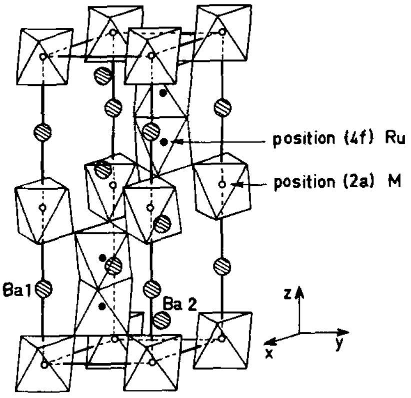

FIG. 1. Unit cell of the ordered hexagonal $BaTiO_3$-type structure of $Ba_3Ru_2MO_9$.

susceptibility measurements have also been reported for $Ba_3Ru_2NiO_9$ by Byrne and Moeller (*6*), but the analysis of the results was complicated by the fact that both Ni^{II} and Ru^{V} contribute to the susceptibility. Various interpretations were discussed but it was not possible to fit the data 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.

Another ruthenium cluster system for which magnetic susceptibility data have been interpreted in terms of an $S = 0$ ground state, is that adopted by the compound Na_3RuO_4 (*7*). The crystal structure of this compound features tetranuclear $(Ru_4O_{16})^{12-}$ clusters isolated entirely from one another by NaO_6 octahedra (*8*, *9*). However, in a recent Mössbauer study we showed conclusively that the published interpretation of magnetic susceptibility data in terms of tetranuclear intracluster antiferromagnetism was incorrect, and concluded that Na_3RuO_4 displays antiferromagnetic three-dimensional long-range order. In addition, between 25 and 30 K motional narrowing of the spectrum was seen, which was attributed to a slow spin–spin relaxation within the crystal field levels of the $^4A_{2g}$ ground state of the Ru^{V} ion (*10*). In the light of these results and bearing in mind the irregularities below 60 K in the published magnetic susceptibility data for the binuclear clusters, it seemed prudent to check their magnetic properties in the low-temperature region by ^{99}Ru Mössbauer spectroscopy. In this paper we report measurements at 4.2 K for the compounds $Ba_3Ru_2MO_9$ (M = Mg, Ca, Sr; Co, Ni, Cu, Zn; and Cd). The Co, Cu, and Zn compounds are new phases prepared recently by Darriet and co-workers (private communication) in Bordeaux, and we are grateful to them for supplying samples and some unpublished magnetic susceptibility data.

Experimental

Samples of all the compounds were kindly provided by Dr. J. Darriet. The methods used in the preparation of the Mg, Ca, Sr, and Cd phases have been outlined (*5*), and similar techniques were used to prepare the other compounds. The Mössbauer spectra were recorded using techniques described previously (*10*), 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 90-keV resonances obtained with this absorber and the various radioactive sources were found to be 0.25 ± 0.01 mm sec^{-1}. Sample thicknesses were ~400 mg cm^{-2} of compound.

Results and Discussion

$Ba_3Ru_2MO_9$ (M = Ca, Sr, and Cd)

The spectra at 4.2 K for the Ca, Sr, and Cd compounds are shown in Fig. 2 and consist of symmetrical single lines, consistent with the presence of unique ruthenium environments and cationic ordering in the face-shared octahedra of the hexagonal barium titanate structure. The solid curves through the data points represent computed least-squares fits

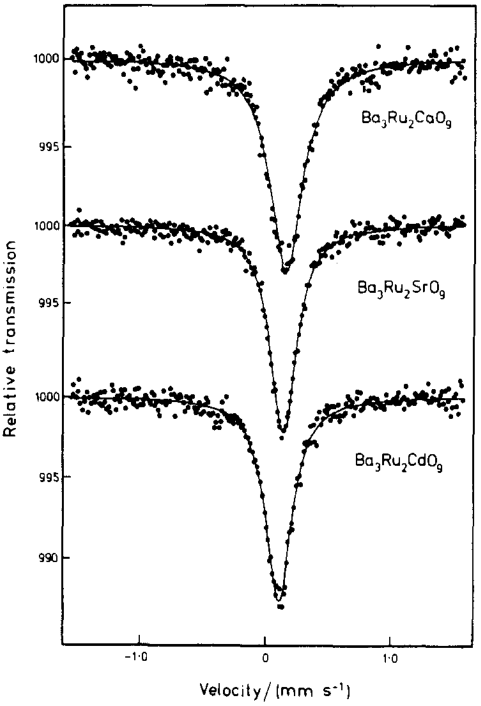

FIG. 2. Mössbauer spectra at 4.2 K for $Ba_3Ru_2MO_9$ (M = Ca, Sr, and Cd). The computed values of the baseline are 4.87×10^6, 5.07×10^6, and 5.28×10^6 counts, respectively.

of single Lorentzian lines and the derived parameters are listed in Table I. The chemical isomer shifts, δ, lie in the range 0.097–0.145 mm sec^{-1} relative to ruthenium metal, which is typical for ruthenium in the +5 oxidation state. Published values of δ for oxide systems containing Ru^V range from +0.039 mm sec^{-1} for Na_3RuO_4 (*10*) to +0.18 mm sec^{-1} for Ca_2EuRuO_6 (*11*). There are no resonances with chemical isomer shifts in the region of −0.30 mm sec^{-1}, which rules out any substantial ruthenium(IV) content and associated oxygen deficiencies.

Close inspection of the chemical isomer shift data in Table I reveals that there are measurable differences in the values for the three compounds but no apparent correlation between this parameter and the nature of the M^{II} cation. At first sight this is perhaps surprising because one might have expected a monotonic increase in δ with increase in effective ionic radius of the M^{II} cation. This follows because an increase in the effective ionic radius of M^{II} should be accompanied by a decrease in M–O covalency and, in turn, an increase in Ru–O covalency, which for ^{99}Ru should lead to an increase in chemical isomer shift (*10*). This argument would require the Sr compound to have the largest chemical isomer shift and not the Ca compound as observed. A possible explanation is that the discrepancy is associated with the monoclinic distortion known (*5*) to exist in the unit cell of the Sr compound. The accompanying distortion of the RuO_6 octahedra adversely affects the overlap of the half-filled $4d(t_{2g})$ orbitals pointing toward the edges of the shared face, and as a result there is a dramatic reduction in both the spectroscopic splitting factor, g, and the exchange integral, J. By the same token the reduced overlap could cause increased localization of $4d$ electron density on the ruthenium, with a consequent decrease in s electron density at the ruthenium nucleus and a reduced chemical isomer shift, as observed. One might perhaps have expected such a structural distortion to have had a greater effect on the quadrupole interaction than on the chemical isomer shift. In the event, there is no detectable quadrupole splitting for any of these three compounds, consistent with the presence of the $4d(t_{2g}^3)$ half-filled shell of Ru^V, and the observed linewidth for the Sr compound is in fact narrower than that for the Ca analogue (0.256 compared with 0.319 mm sec^{-1}).

The absence of magnetic hyperfine splitting in the Mössbauer spectra of these three compounds indicates that they do not exhibit long-range three-dimensional magnetic order at 4.2 K and, as outlined below, is entirely consistent with the published interpretation of their magnetic susceptibility data (*5*). The magnetic data have been interpreted in terms of a model involving spin-coupled binuclear clusters with $S = 0$

TABLE I

^{99}Ru Mössbauer Parameters at 4.2 K for the Phases $Ba_3Ru_2MO_9$

Phase	Electronic configuration of M^{II}	Effective ionic radius of M^{II},[a] IR (pm)	Chemical isomer shift,[b] δ (mm sec^{-1})	Magnetic flux density, B (T)	Linewidth, Γ (mm sec^{-1})	χ^2 (df)[c]
$Ba_3Ru_2CaO_9$	$3p^6$	100	0.145(2)	0	0.319(7)	295(250)
$Ba_3Ru_2SrO_9$	$4p^6$	118	0.131(2)	0	0.256(4)	209(250)
$Ba_3Ru_2CdO_9$	$4d^{10}$	95	0.097(2)	0	0.252(5)	271(250)
$Ba_3Ru_2MgO_9$	$2p^6$	72	0.074(20)	44.6(4)	0.53(5)	352(236)
			0.074(20)	44.8(4)	0.5[d]	352(237)
$Ba_3Ru_2ZnO_9$	$3d^{10}$	74	0.034(30)	35.9(8)	1.23(19)	244(237)
			0.048(20)	38.7(4)	0.5[d]	261(238)
$Ba_3Ru_2CoO_9$	$3d^7$	74.5	0.080(40)	51.1(9)	0.74(13)	204(241)
			0.062(20)	51.6(6)	0.5[d]	209(242)
$Ba_3Ru_2NiO_9$	$3d^8$	69	0.007(20)	31.8(5)	0.68(9)	220(236)
			0.009(20)	32.5(4)	0.5[d]	224(237)
$Ba_3Ru_2CuO_9$	$3d^9$	73	0.057(40)	44.7(8)	0.58(11)	155(236)
			0.056(30)	45.0(7)	0.5[d]	155(237)

[a] Values taken from R. D. Shannon, *Acta Crystallogr. Sect. A* **32**, 751 (1976).
[b] Relative to ruthenium metal.
[c] df = degrees of freedom.
[d] Fixed parameter.

ground states, though there were deviations from the expected behavior at $T < 60$ K. Instead of decreasing to zero as would be expected for such an isolated binuclear system, the susceptibility increased rapidly according to a Curie–Weiss law. There are several possible explanations for this behavior, perhaps the most obvious being that the phases are slightly oxygen deficient and contain traces of paramagnetic Ru^{IV} ions. On the other hand, Darriet *et al.* (*5*) have suggested that the behavior could perhaps be explained by the presence of extremely small numbers (ca. 0.1%) of uncoupled Ru^{V} ($S = 3/2$) ions. Implicit in this model is the assumption that the vast majority of the ruthenium ions would remain in spin-coupled dimers having $S = 0$ ground states, which for reasons discussed in detail elsewhere (*10*) cannot lead to magnetic hyperfine splitting in the Mössbauer spectrum. Any uncoupled Ru^{V} ions would remain undetected in the Mössbauer spectrum because of their low concentration. Their model is therefore also entirely consistent with the present Mössbauer data.

An alternative explanation for the pronounced increase in the magnetic susceptibility of these phases below $T = 60$ K is that they could be low-dimensional with more than one transition temperature. The structure does not rule out the possibility of the binuclear intracluster interactions giving way, at progressively lower temperatures, first of all to interactions of a predominantly one-dimensional nature along the chain, and finally to three-dimensional interactions. Thus the increase in magnetic susceptibility at $T < 60$ K may reflect the growing importance of superexchange interactions via the corner-shared MO_6 octahedra (M = Ca, Sr, or Cd). It is clear, however, from the absence of magnetic hyperfine splitting in the Mössbauer spectra of these three compounds that their three-dimensional ordering temperatures lie below 4.2 K.

$Ba_3Ru_2MO_9$ (M = Mg and Zn)

The spectra at 4.2 K for the Mg and Zn compounds are shown in Fig. 3, and are clearly magnetically split. This result is unexpected and indicates that the low-temperature magnetic behavior of these compounds is quite different from that of the compounds discussed in the previous section. It has only proved possible to obtain satisfactory fits with a single 18-line magnetic hyperfine pattern by allowing the component linewidth to increase beyond its natural value. The results are given in Table I, which reveals that the computed linewidths for the Mg and Zn compounds are 0.53 and 1.23 mm sec^{-1} compared with the value of 0.25 mm sec^{-1} recorded with this source and an absorber of natural ruthenium metal. It is still possible to obtain good fits with the linewidth constrained to a value of 0.5 mm sec^{-1} (as shown by the alternative set of computed data in Table I), but reducing it further causes considerable increases in χ^2. For whatever reason it is therefore clear that the data do not correspond to unique ruthenium environments experiencing static magnetic hyperfine fields.

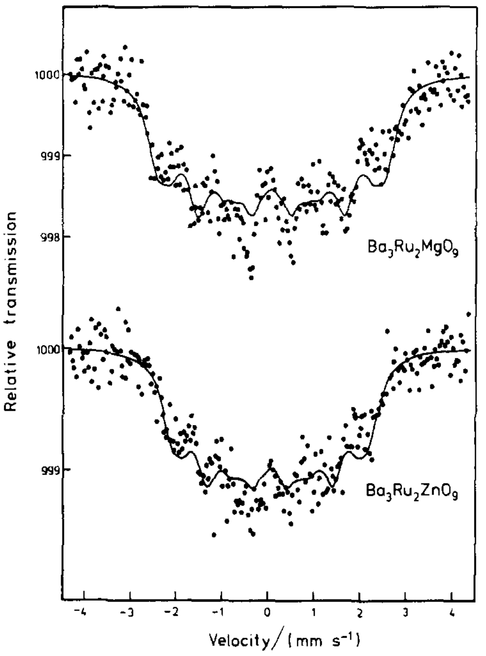

FIG. 3. Mössbauer spectra at 4.2 K for $Ba_3Ru_2MO_9$ (M = Mg and Zn). The component linewidths were fixed at $\Gamma = 0.5$ mm sec^{-1} in these curve fits, and the computed values of the baseline are 19.75×10^6 and 40.16×10^6 counts, respectively.

The chemical isomer shifts for both compounds are within the range of values observed for Ru^V though they are somewhat smaller than those observed for the Ca, Sr, and Cd compounds. This is entirely consistent with increased M–O covalency associated with the smaller ionic size of Mg^{II} and Zn^{II} compared with Ca^{II}, Sr^{II}, and Cd^{II} which leads in turn to reduced Ru–O covalency and decreased chemical isomer shifts as discussed earlier.

The observation of magnetic hyperfine splitting in the Mössbauer spectra of these compounds is intriguing and implies either that the materials are magnetically ordered or that the ruthenium(V) spins are paramagnetic but are relaxing very slowly compared with the Mössbauer excited state lifetime of 2×10^{-8} sec. This poses problems because the magnetic susceptibility data, both for $Ba_3Ru_2MgO_9$ (*4*, *5*) and $Ba_3Ru_2ZnO_9$ (Darriet and co-workers, private communication), have been interpreted satisfactorily on the basis of the models discussed earlier for the Ca, Sr, and Cd compounds, though it should be noted that much higher concentrations (ca. 2.5%) of isolated Ru^V ions were required to explain the temperature dependence of the magnetic susceptibility data at $T < 60$ K. According to this model an overwhelming number of Ru^V ions in both compounds should exist in the $S = 0$ ground state at 4.2 K, which cannot show a magnetic interaction either from long-range magnetic order or as a result of slow paramagnetic relaxation. We are therefore forced to conclude that the isolated cluster model does not correctly describe the magnetic properties of these materials at 4.2 K, and that the pronounced increase in magnetic susceptibility at low temperature must stem from factors other than, or in addition to, the presence of uncoupled ruthenium ions.

In seeking an explanation for the magnetic splitting it should be noted that the isolated cluster model does provide an adequate description of the magnetic behavior in the high-temperature region ($T > 60$ K), where the susceptibility rises steadily with increase in temperature, passes through a broad maximum in the region of 400 K, and then diminishes as expected for spin-coupled dimers. There is therefore little doubt that this compound features ruthenium dimers in face-shared octahedra, and for reasons discussed in detail elsewhere *(10)* slow paramagnetic relaxation at 4.2 K is most unlikely for such a system, even if the ground state has $S > 0$. It is therefore reasonable to conclude that these compounds exhibit cooperative magnetic ordering at 4.2 K. This implies that Ru–O–M–O–Ru magnetic superexchange interactions via the diamagnetic, corner-shared MO_6 octahedra ($M =$ Mg or Zn) compete with the direct Ru–Ru antiferromagnetic intracluster interactions and are dominant at low temperatures. Magnetic interactions involving more than one intervening diamagnetic ion are not without precedent in ruthenium oxide chemistry; indeed our own recent work has revealed several such systems. The case of Na_3RuO_4 has already been referred to *(10)* and other examples include the ordered ruthenium(V) perovskites M_2LnRuO_6 ($M =$ Ca, Sr, or Ba; $Ln =$ Y, La, or Eu) *(11)* and $BaLaMRuO_6$ ($M =$ Mg or Zn) ((*1*), and references therein). The absence of such magnetic ordering in the present compounds $Ba_3Ru_2MO_9$, where $M =$ Ca, Sr, and Cd, suggests that the strength of the exchange interaction is crucially dependent on the ionic size of the M^{II} cation, as this is seen (Table I) to increase from ca. 70 pm for Mg^{II} and Zn^{II} to ca. 100 pm for Ca^{II}, Sr^{II}, and Cd^{II}.

We pointed out earlier that the magnetically split spectra for the Mg and Zn compounds cannot be interpreted on the basis of unique ruthenium environments experiencing static hyperfine fields. Another unusual feature of the data is that the computed values of the magnetic flux density (44.8 and 38.7 T, respectively, for the Mg and Zn compounds) are much smaller than those observed previously for Ru^V in oxide systems. Apart from the value of 52.9 T for Sr_2RuFeO_6 *(12)*, these fall in the narrow range 56.0–59.5 T ((*1*), and references therein; (*10*, *11*)). A possible explanation which needs to be considered is that the samples might be oxygen deficient with small admixtures of Ru^{IV}. The original sample of $Ba_3Ru_2MgO_9$ prepared in air by Callaghan *et al.* *(4)* was shown by chemical analysis to contain only 80% Ru^V, but no special precautions seem to have been taken during the preparation to reduce oxygen deficiency. The samples used in the present study were all synthesized in an atmosphere of oxygen, annealed for long periods, and cooled slowly in an attempt to avoid this problem. The Mössbauer spectra for the Ca, Sr, and Cd compounds show quite clearly that Ru^{IV} is absent, and there is therefore no reason to suspect that it might be present in the Mg and Zn compounds. Ru^{IV} in a magnetically ordered oxide is usually characterized by a chemical isomer shift in the region of -0.3 mm sec^{-1}, and a magnetic field of flux density ca. 36 T *(13)*. Substantial amounts of ruthenium in this oxidation state might therefore be expected to cause asymmetry in the Mössbauer spectrum, but this is not observed (Fig. 3). Moreover, provided there were no electronic averaging effects, one would still expect to see components corresponding to the full Ru^V hyperfine field, but these are absent. We therefore conclude that the line broadening and reduced fields in the spectra of the Mg and Zn compounds are due to causes other than oxygen deficiency.

As discussed elsewhere (*10*), the ground state of the $S = 3/2$ Ru^V ion is analogous to the $S = 5/2$ ground state of Fe^{III} in that orbital and dipolar contributions to the flux density of the hyperfine field are small, and the latter is not expected to vary substantially with environment. However, reductions can be caused by covalent overlap and it is possible that the low values observed for the present compounds stem from the existence of Ru–Ru bonds within the $(Ru_2O_9)^{8-}$ clusters. An alternative explanation is that the magnetic ordering temperatures of these compounds are very close to 4.2 K, with the result that the observed magnetic flux densities do not represent saturation values. Time-dependent phenomena are also more probable in magnetic oxides at temperatures just below the ordering temperature (*10*), and this may explain the difficulty in fitting the spectra as single hyperfine patterns. The only other example of a magnetic relaxation effect in a ^{99}Ru spectrum is that observed for Na_3RuO_4 (*10*), where motional narrowing of the spectrum was seen between 25 K and the Néel point ($T_N = 30$ K), and attributed to slow spin–spin relaxation within the crystal-field levels of the $^4A_{2g}$ ground state of the Ru^V ion under the influence of the molecular magnetic field. It is therefore possible that $Ba_3Ru_2MgO_9$ and $Ba_3Ru_2ZnO_9$ are showing behavior similar to that in Na_3RuO_4, except of course that the cooperative interactions appear to set in at much lower temperatures. Unfortunately this cannot be confirmed from the magnetic susceptibility data because they feature no definite indications of cooperative transition temperatures. Finally, we note that line-broadening effects at temperatures slightly above the three-dimensional ordering temperature have been discussed recently in terms of one-dimensional magnetic behavior in $Fe(N_2H_5)_2(SO_4)_2$ (*14*) and $KFeCl_3$ (*15*). In the light of our earlier comments it is not possible to rule out a similar explanation for the unusual lineshapes and flux densities, both for the present compounds and for those discussed in the following section. However, further speculation is not justified on the basis of the existing data, and additional measurements over a range of temperatures are needed to help resolve these interesting problems.

$Ba_3Ru_2MO_9$ (M = Co, Ni, and Cu)

The spectra at 4.2 K for the Co, Ni, and Cu compounds (Fig. 4) are also magnetically split, and have been curve fitted in a way similar to those of the Mg and Zn compounds. The computed values for the various parameters are given in Table I; constraining the linewidth to be

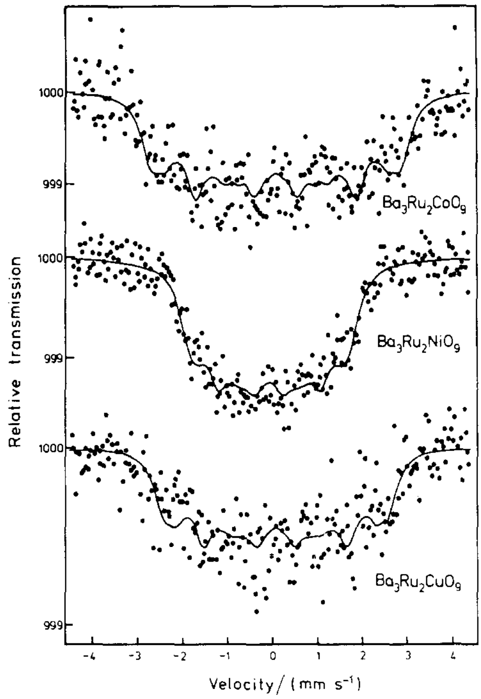

FIG. 4. Mössbauer spectra at 4.2 K for $Ba_3Ru_2MO_9$ (M = Co, Ni, and Cu). The component linewidths were fixed at $\Gamma = 0.5$ mm sec^{-1} in these curve fits, and the computed values of the baseline are 12.15×10^6, 33.14×10^6, and 37.28×10^6 counts, respectively.

0.5 mm sec^{-1} again makes no significant differences to the data, as seen by the second set of figures for each compound. The chemical isomer shifts are all smaller than those recorded for the Ca, Sr, and Cd compounds, consistent with the trends in ionic radii and covalence discussed in the previous section. It is particularly noteworthy that the Ni compound, which contains the smallest M^{II} cation, also gives the smallest chemical isomer shift. The value of +0.009 mm sec^{-1} is, in fact, the smallest so far observed for any ruthenium(V) compound, but it is still well beyond the Ru^{IV} range.

The observation of magnetic hyperfine splitting for the present compounds is less surprising than the results for the Mg and Zn compounds, because the ruthenium clusters are no longer magnetically isolated. Instead, the transition metal cations present in the corner-shared octahedra provide a convenient pathway for magnetic superexchange interactions. The result is entirely consistent with magnetic susceptibility measurements (Darriet and co-workers, private communication), which reveal that these three compounds exhibit long-range antiferromagnetic order with Néel temperatures in the region of 120 K.

The details of the results are more difficult to interpret. The curve-fitted linewidths are again broad, but considering that the Néel points are so high, it is unlikely that these can be explained in terms of time-dependent phenomena. The observed flux densities also vary widely from 32.5 T for the Ni compound, through 45.0 T for the Cu compound, to 51.6 T for the Co compound. The value for the Ni compound is particularly low, and is more typical of Ru^{IV} than Ru^{V}, though this possibility is not consistent with the chemical isomer shift data. As these measurements were made at temperatures far below the Néel points, it is likely that the flux densities have reached their saturation values. A possible explanation for the low values and the wide variation from compound to compound is that the actual flux densities at the ruthenium nuclei have contributions from fields transferred from the paramagnetic ions in the corner-shared octahedra. Additional measurements over a range of temperatures should throw further light on the problem.

Acknowledgments

We thank Professor P. Hagenmuller and Dr. J. Darriet for communicating their results on some of these compounds prior to publication, Dr. T. C. Gibb for helpful discussions during the course of the work, the Spanish Government for a postdoctoral fellowship (to I.F.), and the S.R.C. for financial support.

References

1. I. Fernandez, R. Greatrex, and N. N. Greenwood, *J. Solid State Chem.* **32**, 97 (1980).
2. R. D. Burbank and H. T. Evans, *Acta Crystallogr.* **1**, 330 (1948).
3. P. C. Donohue, L. Katz, and R. Ward, *Inorg. Chem.* **5**, 339 (1966).
4. A. Callaghan, C. W. Moeller, and R. Ward, *Inorg. Chem.* **5**, 1572 (1966).
5. J. Darriet, M. Drillon, G. Villeneuve, and P. Hagenmuller, *J. Solid State Chem.* **19**, 213 (1976).
6. R. C. Byrne and C. W. Moeller, *J. Solid State Chem.* **2**, 228 (1970).
7. M. Drillon, J. Darriet, and R. Georges, *J. Phys. Chem. Solids* **38**, 411 (1977).
8. J. Darriet and A. Vidal, *C.R. Acad. Sci. Paris Ser. C* **227**, 1235 (1973).
9. J. Darriet and J. Galy. *Bull. Soc. Fr. Minéral. Cristallogr.* **97**, 3 (1974).
10. T. C. Gibb, R. Greatrex, and N. N. Greenwood, *J. Solid State Chem.* **31**, 153 (1980).
11. R. Greatrex, N. N. Greenwood, M. Lal, and I. Fernandez, *J. Solid State Chem.* **30**, 137 (1979).
12. T. C. Gibb, R. Greatrex, N. N. Greenwood, and K. G. Snowdon, *J. Solid State Chem.* **14**, 193 (1975).
13. T. C. Gibb, R. Greatrex, N. N. Greenwood, and P. Kaspi, *J. Chem. Soc. Dalton*, 1253 (1973).
14. C. Cheng, H. Wong, and W. M. Reiff, *Inorg. Chem.* **16**, 819 (1977).
15. V. Petrouleas, A. Simopoulos, and A. Kostikas, *Phys. Rev. B* **12**, 4675 (1975).