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A Study of the Ruthenium(V) Perovskites $M_2Ln\mathrm{RuO}_6$ ($M = \mathrm{Ca}$, $Ln = \mathrm{Y}$, La, or Eu; $M = \mathrm{Sr}$, $Ln = \mathrm{Y}$; $M = \mathrm{Ba}$, $Ln = \mathrm{La}$ or Eu) by ^{99}Ru Mössbauer Spectroscopy and Other Techniques

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Ruthenium-99 Mössbauer spectroscopy has been used in conjunction with other techniques to examine the new perovskite phases $\mathrm{Ca}_2Ln\mathrm{RuO}_6$ ($Ln = \mathrm{Y}$, La, or Eu) and the recently reported analogous strontium and barium compounds $M_2Ln\mathrm{RuO}_6$ ($M = \mathrm{Sr}$, $Ln = \mathrm{Y}$; $M = \mathrm{Ba}$, $Ln = \mathrm{La}$ or Eu). At 4.2°K the spectra show widely split magnetic hyperfine patterns ($B = 56$–60 T) having chemical isomer shifts in the range 0.13–0.18 mm sec^{-1} relative to ruthenium metal, thereby confirming the presence of magnetically ordered ruthenium(V) ions in these phases. The computed linewidths for the yttrium compounds are close to the natural value, indicative of unique ruthenium environments and the existence of crystallographic order between Ru$^{\mathrm{V}}$ and Y$^{\mathrm{III}}$ ions on the B-sites. This is further corroborated by the observation of superlattice reflections in the X-ray powder diffraction pattern of $\mathrm{Ca_2YRuO_6}$. Superlattice reflections are also observed for $\mathrm{Ca_2LaRuO_6}$, $\mathrm{Ba_2LaRuO_6}$, and $\mathrm{Ba_2EuRuO_6}$. The Mössbauer spectra for the barium compounds feature sharp paramagnetic components in addition to the magnetically split ruthenium(V) resonances, and possible explanations for these unusual results are discussed. Magnetic susceptibility measurements above 80°K show that all the compounds follow a Curie–Weiss law with negative paramagnetic Curie temperatures, indicative of antiferromagnetism. Measurements down to 4.2°K for the calcium compounds reveal Néel temperatures in the region of 15°K when $Ln = \mathrm{Y}$ or La, whereas $\mathrm{Ca_2EuRuO_6}$ appears to be ferrimagnetic. Electrical resistivity measurements on compacted powders indicate that the materials are not metallic conductors. Mössbauer and powder X-ray diffraction measurements for the phase reported as $\mathrm{Sr_2LaRuO_6}$ indicate that it is in fact a mixture of $\mathrm{Sr_2RuO_4}$ and a solid-solution phase of the type $\mathrm{Sr_2La}_x\mathrm{Ru}_{1-x}\mathrm{O}_4$.

Introduction

Donohue and McCann have recently described the preparation of novel automobile emission control catalysts of formula $M_2Ln\mathrm{RuO}_6$ ($M = \mathrm{Sr}$ or Ba, $Ln = \mathrm{Y}$, rare earth, or Bi), some of which crystallize with the ordered perovskite structure and are thought to contain ruthenium in the pentavalent state (*1*). The magnetic properties of these compounds are of special interest because oxide phases containing ruthenium (V) are rare and superexchange interactions between ruthenium ions in the ordered perovskite structure can occur only through the intermediary O–Ln–O, where Ln is in some cases a diamagnetic cation (*2*).

The presence of ruthenium(V) in these phases was suggested by oxygen analysis and analysis of $\mathrm{Cl_2}$ generated by reaction with HCl, and further corroborated by comparison of their cell volumes with those of related perovskites. In order to

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establish unequivocally the existence of ruthenium(V) and to obtain information about their magnetic properties we have studied a selection of these materials by ^{99}Ru Mössbauer spectroscopy. In addition we have synthesized several new calcium analogs, and have investigated their properties also.

The work is part of a systematic study of ternary and quaternary ruthenium oxides, designed to lead to a better understanding of the magnetic properties of the 4*d* transition series. In previous studies we have highlighted the remarkable difference in magnetic properties for the ternary oxides $CaRuO_3$, $SrRuO_3$, and $BaRuO_3$ (*3, 4*) and have investigated a number of solid-solution perovskite phases derived from them by substituting either at the *A*-site, e.g., $Ca_xSr_{1-x}RuO_3$ (*5*), $La_xCa_{1-x}RuO_3$ (*6*), and $La_xSr_{1-x}RuO_3$ (*6*), or at the *B*-site, e.g., $SrIr_xRu_{1-x}O_3$ (*4*), $SrMn_xRu_{1-x}O_3$ (*4*), and $SrFe_xRu_{1-x}O_{3-y}$ (*7*). The latter study provided the first examples of spectra of ruthenium(V) in an oxide lattice, and more recently we have studied the sodium ruthenium oxides Na_3RuO_4 and $Na_4Ru_2O_7$ in which the ruthenium is also pentavalent (*8, 9*). Further work on novel ruthenium(V) systems is in progress and will be reported elsewhere (*10*). Our work has demonstrated that the chemical isomer shift, δ, and the magnetic flux density, *B*, are diagnostic of the formal ruthenium oxidation state in oxide systems, and has established ^{99}Ru Mössbauer spectroscopy as an invaluable tool for studying the electronic and magnetic properties of materials of this type.

In this paper we describe not only the Mössbauer spectra, but also the results of magnetic susceptibility, electrical resistivity, and powder X-ray diffraction measurements on the new compounds Ca_2LnRuO_6 (*Ln* = Y, La, or Eu), and the phases reported by Donohue and McCann as Sr_2LnRuO_6 (*Ln* = Y or La), and Ba_2LnRuO_6 (*Ln* = La or Eu).

Experimental

The compounds were prepared by heating the appropriate alkaline earth carbonate and rare earth oxide together with ruthenium metal or RuO_2 in platinum vessels at 1000–1200°C in air. The products were characterized by X-ray diffraction using a Philips powder diffractometer and Cu$K\alpha$ radiation ($\lambda = 154.18$ pm). Cell dimensions were derived from least-squares refinement of the *d*-values. Electrical resistivity was measured on compacted powder samples at room temperature using a simple two-probe technique.

The ^{99}Ru Mössbauer spectra were recorded at 4.2°K using techniques described previously (*8*). The experimental data were stored in a MEDA multichannel analyzer and computed using programs developed by Dr. T. C. Gibb. All chemical isomer shift data are quoted relative to an absorber of natural ruthenium metal at 4.2°K having a thickness $140\ \mathrm{mg\ cm^{-2}}$. The experimental linewidth of the radioactive source measured against this absorber was found to be $0.25 \pm 0.01\ \mathrm{mm\ sec^{-1}}$. Sample thicknesses were typically $500\ \mathrm{mg\ cm^{-2}}$ of compound.

Magnetic susceptibilities were measured for all the samples with a Gouy balance over the temperature range 80–300°K, and for the new samples Ca_2LnRuO_6 (*Ln* = Y, La, or Eu) with a Faraday balance over the temperature range 4.2–300°K. They were calibrated against $Hg[Co(CNS)_4]$ for which the magnetic susceptibility at 290°K is $207(\pm 1.0) \times 10^{-12}\ \mathrm{m^3\ mole^{-1}}$ [$16.44(\pm 0.08) \times 10^{-6}\ \mathrm{emu\ mole^{-1}}$].

Crystallographic Data

The X-ray powder diffraction data for the new phases Ca_2YRuO_6 and Ca_2LaRuO_6 (Table I) could be indexed entirely on the basis of orthorhombically distorted perovskite cells with the lattice parameters quoted in Table II. The patterns were similar to that

TABLE I

X-Ray Powder Diffraction Data for Ca_2LaRuO_6

I_{obs}	hkl	d_{obs}/pm	d_{calc}/pm
16	101	471.3	471.3
16	011	460.4	459.5
13	111	360.4	360.6
31	200	290.8	290.9
100	112	284.9	284.7
31	020	279.7	280.0
9	201	273.4	273.5
5	211	245.5	245.8
10	121	240.5	240.7
4	202	235.9	235.6
4	022	229.8	229.7
8	113	223.5	232.2
30	220	201.9	201.7
8	203	196.7	197.1
10	311	178.6	178.7
17	312	166.7	166.7
15	204	165.3	165.3
22	132	162.7	162.6
6	313	151.2	151.3
11	224	142.3	142.4
6	040	140.1	139.9
6	314	135.4	135.4
10	421	127.4	127.4
10	244	106.9	106.8

described for Ca_2CoWO_6 (*11*) and featured reflections characteristic of crystallographic order on the sublattice of the *B* cations. In contrast, the new phase Ca_2EuRuO_6 gave a pattern which could be indexed on the basis of a pseudocubic perovskite cell with a cell edge approximately twice that of the simple perovskite cell, and a slight tetragonal distortion. Despite the doubling of the cell edge, the presence of reflections for which *h*, *k*, and *l* are not all even or all odd implies that the pseudocubic cell is simple cubic and not face-centered cubic like the ordered perovskite structure described by Steward and Rooksby (*12*). Similar results have been reported by Galasso and Darby (*13*) for compounds of the type La_2MRuO_6, which we have also studied by ^{99}Ru Mössbauer spectroscopy (*10*).

The orthorhombically distorted perovskite Sr_2YRuO_6 gave a pattern which could be indexed satisfactorily using the cell dimensions reported by Donohue and McCann (*1*). For this compound the distortion is so small that any superlattice lines remain unresolved and crystallographic order on the *B*-cation site is not apparent from the powder data. The X-ray diffraction pattern for the phase reported by Donohue and McCann as Sr_2LaRuO_6 was tentatively indexed by them on the basis of a hexagonal cell having the parameters listed in Table II. The material prepared in our laboratory has an identical X-ray pattern but our Mössbauer and X-ray data suggest strongly that it consists of Sr_2RuO_4 together with the compound $Sr_2La_{0.5}Ru_{0.5}O_4$ or possibly a

TABLE II

Lattice Parameters for the Perovskite Phases $M^{II}_2Ln^{III}Ru^{V}O_6$

Phase	a/pm	b/pm	c/pm	V/nm^3
Ca_2YRuO_6	548.5(8)	572.6(7)	789.7(9)	0.2480(5)
Ca_2LaRuO_6	581.7(16)	560.0(15)	803.8(70)	0.2618(18)
Ca_2EuRuO_6	796.8(10)	796.8(10)	787.2(10)	0.4998(19)
Sr_2YRuO_6[a]	575.2(1)	577.3(1)	815.8(1)	
Sr_2LaRuO_6[a,b]	1720(2)		820.9(15)	
Ba_2LaRuO_6	854.5(5)			0.6239(7)
Ba_2EuRuO_6	840.5(5)			0.5938(11)

[a] Data from Ref. (*1*).

[b] Our results suggest that this material is in fact a mixture of Sr_2RuO_4 and $Sr_2La_{0.5}Ru_{0.5}O_4$ or a related phase based on the solid-solution system $Sr_2La_xRu_{1-x}O_4$.

solid solution of the type $Sr_2La_xRu_{1-x}O_4$. Further work is in progress on the latter system and will be reported in due course.

The phases Ba_2LnRuO_6 (*Ln* = La or Eu) were both found to adopt the cubic ordered perovskite structure with lattice parameters (Table II) double those reported by Donohue and McCann (*1*). The superlattice lines were extremely weak, however, and were only apparent in patterns recorded at very slow scanning speeds.

Electrical Resistivity

Electrical resistivities of compacted powder samples at room temperature are recorded in Table III. Although these values are likely to be somewhat higher than the true values for single crystals, the results demonstrate clearly that these phases are not metallic conductors. This behavior is therefore in sharp contrast to that displayed by $CaRuO_3$ and $SrRuO_3$ for which measurements on single crystals gave values of 2.5×10^{-4} and 2.8×10^{-4} Ω-cm, respectively, at 300°K (*14*). The metallic conductivity in these compounds was attributed to the favorable overlap of ruthenium *d* orbitals of t_{2g} symmetry with oxygen p_π orbitals leading to the formation of a partially filled π^* band. Introduction of Y^{III}, La^{III}, or Eu^{III} in place of Ru^{IV} in $CaRuO_3$, $SrRuO_3$, and $BaRuO_3$ replaces the Ru^{IV}–O–Ru^{IV} interactions by interactions of the type Ru^V–O–Ln^{III}–O–Ru^V thereby preventing the formation of such bands. Moreover, the *Ln*–O and Ru–O energy levels will presumably be too disparate to allow for significant mixing. Similar behavior has been reported for the cubic ordered perovskite Ba_2YReO_6 which is a semiconductor ($\rho = 30$ Ω-cm) with an activation energy of 0.13 eV. The semiconduction was presumed to occur by direct Re–Re interactions, but in view of the large separation between the rhenium cations (ca. 550 pm) the activation energy was considered to be surprisingly low (*15*). Activation energies have not been measured for the present compounds.

TABLE III

APPROXIMATE ELECTRICAL RESISTIVITIES FOR COMPACTED POWDER SAMPLES OF THE PHASES $M_2^{II}Ln^{III}Ru^VO_6$

Phase	Electrical resistivity (ρ/Ω-cm)
Ca_2YRuO_6	7.7×10^5
Ca_2LaRuO_6	7.6×10^5
Ca_2EuRuO_6	1.2×10^7
Sr_2YRuO_6	5.9×10^4
Ba_2LaRuO_6	1.9×10^5
Ba_2EuRuO_6	2.3×10^7

Magnetic Susceptibility

The Mössbauer spectra to be presented in the following section clearly establish the existence of long-range magnetic order in these compounds at 4.2°K. In order to obtain further information about the nature of the magnetic interactions, magnetic susceptibilities have been measured with a Gouy balance for all the compounds down to 80°K, and for the new compounds Ca_2LnRuO_6 (*Ln* = Y, La, or Eu) with a Faraday balance down to 4.2°K. Excellent agreement was obtained between the two methods in the common temperature region. The plots of $1/\chi'_M$ vs T are given in Figs. 1 and 2 and the calculated magnetic parameters are listed in Table IV.

All the compounds appear to follow a Curie–Weiss law at high temperatures with negative paramagnetic Curie temperatures, indicating that the long-range magnetic order detected in the Mössbauer measurements stems from antiferromagnetic rather than ferromagnetic exchange interactions. For Ca_2YRuO_6 and Ca_2LaRuO_6 the measurements down to 4.2°K establish definite Néel points, T_N, of 16 and 12°K, respectively, whereas Ca_2EuRuO_6 appears

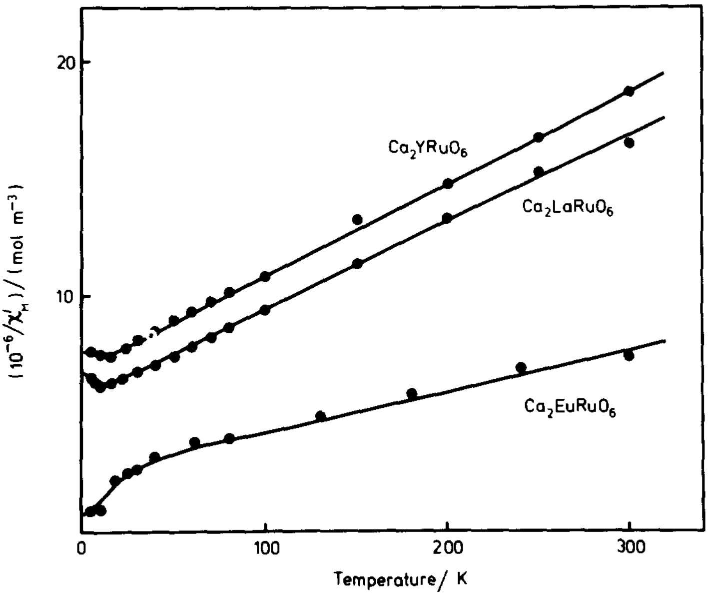

FIG. 1. The temperature variation of the reciprocal susceptibility ($1/\chi'_M$) for the phases Ca_2LnRuO_6 (Ln = Y, La, or Eu), measured with the Faraday balance.

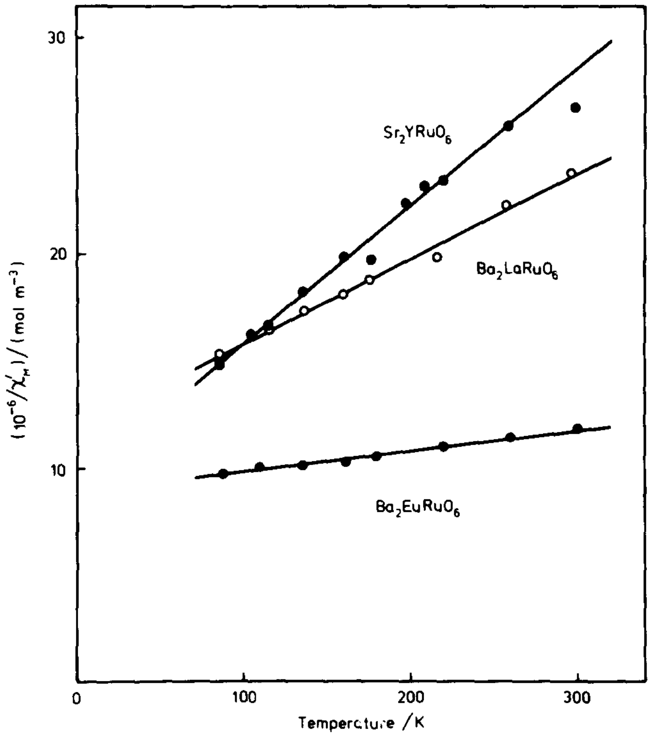

FIG. 2. The temperature variation of the reciprocal susceptibility ($1/\chi'_M$) for the phases Sr_2YRuO_6, Ba_2LaRuO_6, and Ba_2EuRuO_6, measured with the Gouy balance.

TABLE IV

MAGNETIC DATA FOR THE PEROVSKITES $M_2^{\mathrm{II}}Ln^{\mathrm{III}}\mathrm{Ru}^{\mathrm{V}}\mathrm{O}_6$

Phase	$10^6\ C_\mathrm{M}/\mathrm{m}^3\ {}^\circ\mathrm{K\ mole}^{-1}$ [a]	$\mu_\mathrm{eff}/\mu_\mathrm{B}$ [b]	$\theta/{}^\circ\mathrm{K}$ [c]	$T_\mathrm{N}/{}^\circ\mathrm{K}$
$\mathrm{Ca_2YRuO_6}$	25.39	4.02	−176	16
$\mathrm{Ca_2LaRuO_6}$	28.56	4.27	−158	12
$\mathrm{Ca_2EuRuO_6}$	55.85	5.97	−126	~10 [d]
$\mathrm{Sr_2YRuO_6}$	15.42	3.13	−142	<80
$\mathrm{Ba_2LaRuO_6}$	25.13	4.00	−304	<80
$\mathrm{Ba_2EuRuO_6}$	104.72	8.17	−1000	<80

[a] C_M is the molar Curie constant calculated from the linear portion of the plot of $1/\chi'_\mathrm{M}$ vs T. To convert to emu °K mole^{-1} multiply by $10^6/4\pi$.

[b] Effective magnetic moment calculated from the equation $\mu_\mathrm{eff} = 2.83((10^6/4\pi)C_\mathrm{M})^{1/2}$.

[c] θ is the intercept on the temperature axis, extrapolated from the linear portion of the plot of $1/\chi'_\mathrm{M}$ vs T.

[d] $\mathrm{Ca_2EuRuO_6}$ appears to be ferrimagnetic. The value given is the approximate Curie temperature.

to be ferrimagnetic with a Curie temperature in the region of 10°K. Consistent with this, the magnetic susceptibility was found to be field dependent at 4.2 and 10°K, and appropriate corrections have been made to the data at these temperatures. Magnetization measurements would be desirable to establish the value of the saturation moment in both this compound and $\mathrm{Ba_2EuRuO_6}$.

As measurements have been made only up to room temperature, the paramagnetic Curie temperatures given in Table IV may not be particularly accurate, Nevertheless with the inclusion of these θ-values the magnetic moments calculated for the yttrium and lanthanum compounds are more or less independent of temperature in the paramagnetic region, and have values ranging from 3.13 to 4.27 μ_B, in reasonable agreement with the temperature independent value of ca. 3.5 μ_B expected for the t_{2g}^3 configuration of ruthenium(V) (*16*). Attempts to estimate the contributions of each of the paramagnetic ions to the susceptibility in $\mathrm{Ca_2EuRuO_6}$ and $\mathrm{Ba_2EuRuO_6}$ have been less successful, presumably because of complications associated with the close spacing between the two lowest J-levels of the europium(III) ion. If it is assumed that the susceptibilities for ruthenium in these two compounds are the same as those in $\mathrm{Ca_2LaRuO_6}$ and $\mathrm{Ba_2LaRuO_6}$, respectively, the calculated moments for the europium ions are 4.17 and 5.18 μ_B which are higher than the values of 3.4–3.6 μ_B normally observed for europium(III) (*17*).

Mössbauer Measurements

The ^{99}Ru Mössbauer spectra at 4.2°K for the calcium, strontium, and barium compounds are shown in Figs. 3–5, respectively. The calcium compounds $\mathrm{Ca_2}Ln\mathrm{RuO_6}$ (Ln = Y or La) feature magnetically split spectra in which the 18 components resulting from the nuclear $I_g = 5/2 \rightarrow I_e = 3/2$ transition are nearly all distiguishable. The spectrum for the europium analog is similar but less well resolved. A longer counting time would have been desirable but was precluded by the short lifetime of the source ($t_{1/2} =$ 16 d); in general the spectra were accumulated only for a time sufficient to allow the main features to become apparent. The solid lines through the data points are the computed least-squares fits in which the relative intensities have been constrained to their theoretical values as indicated by the

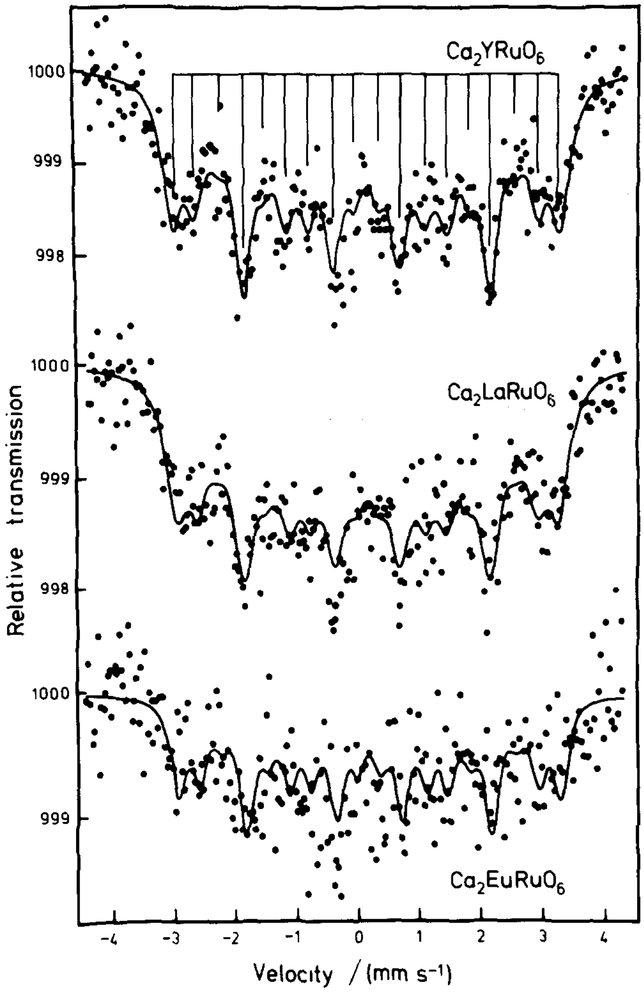

FIG. 3. ^{99}Ru Mössbauer spectra at 4.2°K for Ca_2YRuO_6, Ca_2LaRuO_6, and Ca_2EuRuO_6. The computed values of the baselines are 13.04×10^6, 13.74×10^6, and 8.94×10^6, respectively.

bar diagram in Fig. 3. Sr_2YRuO_6 and Ba_2EuRuO_6 give spectra similar to those of the calcium compounds but "Sr_2LaRuO_6" and Ba_2LaRuO_6 feature sharp paramagnetic components near zero velocity in addition to the magnetically split resonances. In curve fitting these latter spectra an extra Lorentzian line of variable intensity has therefore been included in the analysis.

The computed parameters are given in Table V and reveal that the magnetically split components have flux densities ranging from 56.1 to 59.5 T and chemical isomer shifts from 0.13 to 0.18 mm sec^{-1} relative to ruthenium metal. These values are close to those observed for the magnetically ordered ruthenium(V) oxides $SrFe^{III}_{0.5}Ru^{V}_{0.5}O_3$ ($B = 52.9$ T, $\delta = +0.116$ mm sec^{-1}) (*7*) and Na_3RuO_4 ($B = 58.58$ T, $\delta = +0.039$ mm sec^{-1}) (*9*), and confirm the existence of ruthenium(V) in the new compounds. For comparison, $SrRu^{IV}O_3$ gives a much smaller magnetic hyperfine field of flux density 35.2 T, and a chemical isomer shift of

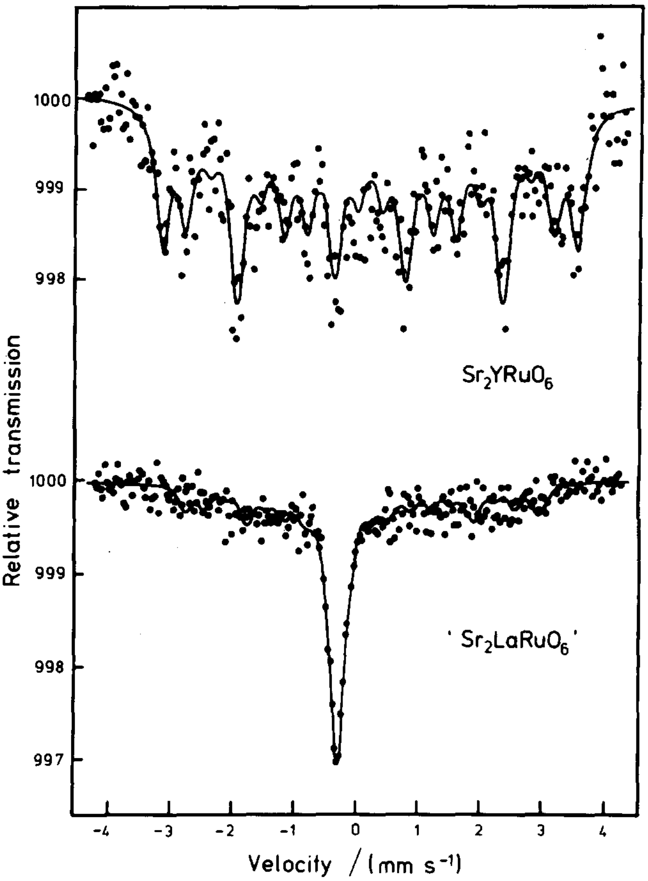

FIG. 4. ^{99}Ru Mössbauer spectra at 4.2°K for Sr_2YRuO_6 and the phase reported by Donohue and McCann as Sr_2LaRuO_6. Our results show this to be a mixture of Sr_2RuO_4 and $Sr_2La_{0.5}Ru_{0.5}O_4$, giving rise to the sharp paramagnetic component and magnetically split pattern, respectively. The computed values of the baselines are 9.16×10^6 and 39.19×10^6, respectively.

-0.33 mm sec^{-1}, which is typical for this oxidation state (*4*). Ruthenium(III) is not known in a magnetic oxide but the low-spin d^5 configuration, having only a single unpaired electron, would be expected to give a field of ca. 17 T; moreover the chemical isomer shifts for this oxidation state fall in the range -0.56 to -0.69 mm sec^{-1} (*6, 8*). It is difficult to put a limit on the amount of Ru^{IV} or Ru^{III} which would be detected in the spectra but the χ^2 values show that they compute extremely well on the basis of Ru^V alone, and this would be unlikely if even a small percentage of the lower oxidation states were present.

Looking more closely at the data in Table V it is apparent that the parameters are relatively insensitive both to the nature of the A-cation and the lanthanide in the B-site. As we have pointed out elsewhere (*7*), this oxidation state has a $4d^3$ configuration with $S = 3/2$ and is akin to iron(III) in that the magnetic flux density should vary little with change in environment. This is certainly the case for the calcium series Ca_2LnRuO_6 (Ln = Y, La, or Eu) for which the magnetic

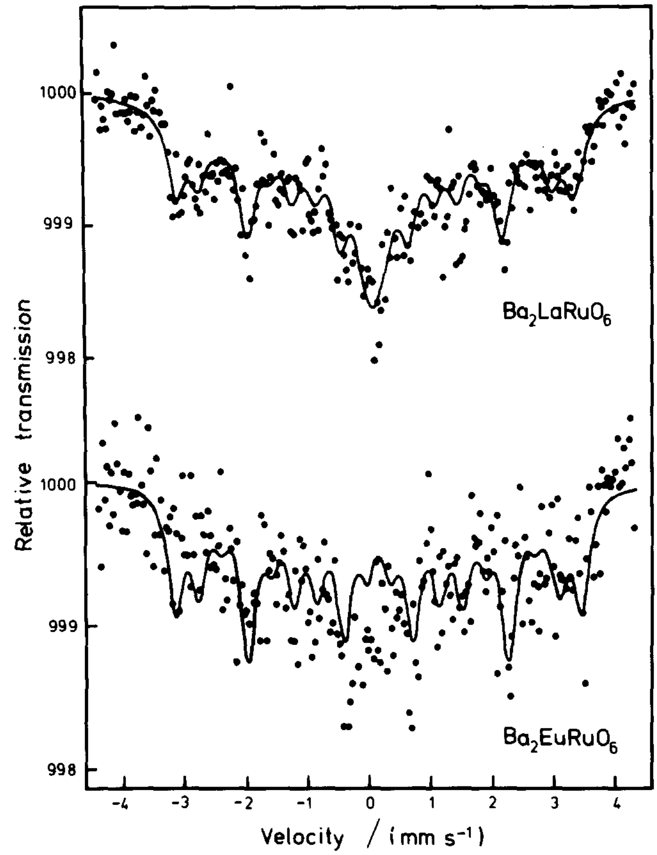

FIG. 5. ^{99}Ru Mössbauer spectra at 4.2°K for Ba_2LaRuO_6 and Ba_2EuRuO_6. The computed values of the baselines are 32.96×10^6 and 12.46×10^6, respectively.

fields are identical within experimental error. The values for these compounds are marginally smaller than those for the strontium and barium analogs and this may reflect the reduction in the exchange field at the ruthenium nucleus caused by the greater Lewis acidity of Ca^{II} compared with Sr^{II} and Ba^{II}.

The remaining parameter of interest in Table V is the linewidth Γ, the computed values of which are seen to vary from 0.29 to 0.58 mm sec^{-1}. Notwithstanding the comments made earlier about the insensitivity of the d^3 configuration to changes in environment, it is nevertheless reasonable to expect very sharp linewidths to occur only for phases exhibiting crystallographic order. The value of 0.29 mm sec^{-1} observed for Sr_2YRuO_6, which is very close to that recorded using an absorber of natural ruthenium metal (0.25 mm sec^{-1}), therefore provides convincing evidence that this material is also an ordered perovskite, though it was not possible to deduce this from the crystallographic data. Furthermore, the largest computed linewidth is for Ca_2EuRuO_6 in which superlattice ordering is not proved. The other compounds studied have all been shown by X-ray crystallography to exhibit order on the B-cation site and of these, Ca_2YRuO_6 and Ba_2LaRuO_6 give relatively narrow linewidths each of 0.37 mm sec^{-1}, whereas Ca_2LaRuO_6 and Ba_2EuRuO_6 give values of 0.43 and 0.52 mm sec^{-1},

TABLE V

MÖSSBAUER PARAMETERS AT 4.2°K FOR THE PEROVSKITES $M_2^{II}Ln^{III}Ru^{V}O_6$

Phase	Chemical isomer shift[a] (δ/mm sec^{-1})	Magnetic flux density (B/T)	Linewidth (Γ/mm sec^{-1})	χ^2 (df)[b]
Ca_2YRuO_6	+0.143±0.010	56.6±0.2	0.37±0.02	261(241)
Ca_2LaRuO_6	+0.145±0.010	56.1±0.3	0.43±0.03	240(241)
Ca_2EuRuO_6[c]	+0.177±0.030	56.5±0.8	0.58±0.09	217(241)
	+0.188±0.010	56.1±0.4	0.30[d]	235(242)
Sr_2YRuO_6	+0.159±0.010	59.5±0.2	0.29±0.02	230(241)
Ba_2LaRuO_6[e]	+0.132±0.030	57.9±0.3	0.37±0.02	263(241)
	+0.110±0.020	0	0.50±0.06	
Ba_2EuRuO_6[c]	+0.154±0.030	59.2±0.7	0.52±0.07	328(241)
	+0.153±0.010	59.3±0.3	0.30[d]	344(242)

[a] Relative to ruthenium metal at 4.2°K.
[b] df = degrees of freedom.
[c] The two rows of data refer to two separate fits to the same spectrum.
[d] Fixed parameter.
[e] The two rows of data refer respectively to the magnetic and paramagnetic components.

respectively. There is evidence, to be discussed later, that Ba_2LaRuO_6 and Ba_2EuRuO_6 may not be completely ordered, and this could account for the observed line broadening. However, it is unwise to place too great a significance on these computed values as the spectra can still be computed satisfactorily with the linewidths constrained to the value of 0.30 mm sec^{-1}, as indicated in Table V.

The magnetic and Mössbauer data presented so far have shown convincingly that the materials reported by Donohue and McCann, and the new series Ca_2LnRuO_6 (Ln = Y, La, or Eu) all exhibit long-range magnetic order at 4.2°K. At first sight this is a surprising result considering that the end-member $CaRuO_3$ is paramagnetic at this temperature, and that the ruthenium ions on the B-site in the present compounds are diluted substantially, in some cases by diamagnetic ions (e.g., Y^{III} or La^{III}). Blasse has shown (*2*) that the dominant magnetic interaction in compounds of this type is a superexchange involving the diamagnetic intermediary O–Ln–O rather than a direct metal–metal interaction (see Fig. 6). The strength of the interaction was found to increase with increasing electron affinity of the diamagnetic B ion, as monitored by the ionization potential of its last electron, and this is also found to be the case for the compounds Ca_2YRuO_6 and Ca_2LaRuO_6 in the present study. The Néel temperatures observed for the two compounds are 16 and 12°K, respectively, and the third ionization potentials for the diamagnetic ions Y^{III} and La^{III} are 20.4 and 19.2 eV. Blasse has also demonstrated that, for a given oxidation state, the 180° M–O–M interaction found in the ideal perovskite structure is an order of magnitude stronger than the M–O–Ln–O–M interaction, though the M–M distance in the former configuration is only half that in the latter (*2*). The sign of the interactions should be the same, however, and for d^3 ions it should be negative (antiferromagnetic) as observed (*18*). The present results demonstrate that the Ru^{V}–O–Ln^{III}–O–Ru^{V} superexchange interaction in the compounds M_2LnRuO_6 is stronger than the Ru^{IV}–O–Ru^{IV} superexchange in $CaRuO_3$, indicating that exchange interactions between ruthenium(V) ions are very much stronger

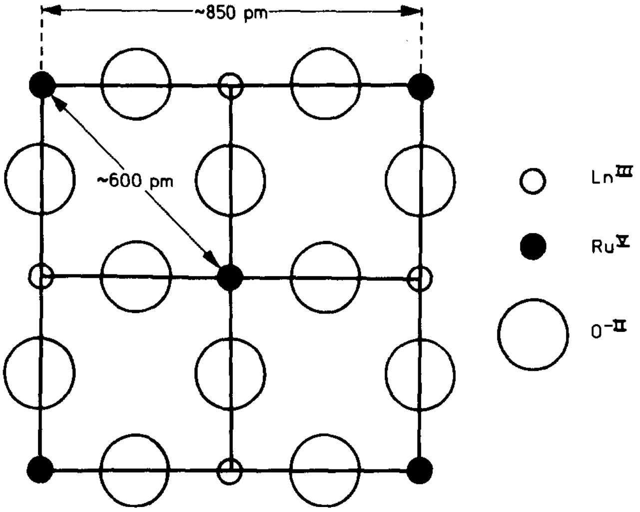

FIG 6. (100) face of the cubic ordered perovskite structure (after Blasse, Ref. (2)). The dominant magnetic interaction is of the type Ru–O–*Ln*–O–Ru rather than the direct Ru–Ru interaction.

than those involving ruthenium(IV). Consistent with this is our recent confirmation of long-range antiferromagnetic order in Na_3RuO_4 (*9*). This compound crystallizes with an ordered NaCl-type structure, with clusters of four fused RuO_6 octahedra isolated entirely from one another by NaO_6 octahedra, such that superexchange interactions between ruthenium ions must take place across intervening NaO_6 octahedra. Nevertheless the compound is antiferromagnetic with a Néel temperature of 30 ± 1°K.

Certain features of the spectra in Figs. 4 and 5 have not yet been discussed in detail. As mentioned earlier, the spectrum of the phase reported by Donohue and McCann as Sr_2LaRuO_6 has a sharp paramagnetic component in addition to a ruthenium(V) magnetic hyperfine pattern, and from the computed value of its chemical isomer shift (-0.26 ± 0.01 mm sec^{-1}) ruthenium(IV) is indicated. A possible explanation is that the compound is oxygen deficient, with a mixture of paramagnetic ruthenium(IV) and magnetically ordered ruthenium(V) ions in the same crystallographic phase. However, the chemical isomer shift of the paramagnetic line is identical to that observed for Sr_2RuO_4 (*6*) and lines characteristic of this phase are present in the powder X-ray diffraction pattern also. The remaining lines in the X-ray pattern correspond closely with those observed (*10*) for the phase $Sr_2La_{0.5}Ru_{0.5}O_4$ and the magnetically split component has Mössbauer parameters similar to those observed for this phase.

The paramagnetic component present in the spectrum of Ba_2LaRuO_6 (Fig. 5) is of a different nature because its chemical isomer shift characterizes it as a ruthenium(V) resonance. It is unlikely to arise from superparamagnetic fine particles at such a low temperature, and other relaxation phenomena seem equally improbable. It could indicate that the sample contains a small amount of a ruthenium(V) impurity phase, though it is not obvious what this might be and there is no sign of it in the X-ray pattern. A possible alternative explanation is that the resonance is associated with regions of crystallographic disorder in an otherwise ordered cubic perovskite phase. The superexchange interactions in the crystallographically ordered phases are in any case quite weak, as evidenced by the low Néel temperature, $T_N = 16°K$, for Ca_2YRuO_6. The effect of disorder would be to introduce ruthenium ions with one or more linkages of the type Ru^V–O–La^{III}–O–La^{III}, for which the superexchange interaction would be even weaker. Such ruthenium ions, being only weakly coupled to the lattice, would be likely to undergo rapid spin relaxation even below the Néel point, thus accounting for the observed paramagnetic component. It should be noted that there is evidence of a similar, though much less intense, paramagnetic component in the spectrum of Ba_2EuRuO_6, but no attempt has been made to curve fit this in detail because of the poor quality of the spectrum.

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