^{99}Ru and ^{151}Eu Mossbauer Spectra of the Ternary Hydrides M_2RuH_6 (M = Ca, Sr, Eu, or Yb)

By **Inmaculada Fernandez, Robert Greatrex,** and **Norman N. Greenwood,*** Department of Inorganic and Structural Chemistry, The University of Leeds, Leeds LS2 9JT

^{99}Ru Mossbauer spectra have been recorded at 4.2 K for the ternary hydrides M_2RuH_6 (M = Ca, Sr, Eu, or Yb), and are consistent with the presence of diamagnetic ruthenium(II) in all four compounds. ^{151}Eu Mossbauer measurements reveal that Eu_2RuH_6 contains magnetically ordered Eu^{II}; the internal field follows an $S = \frac{7}{2}$ Brillouin function with a Curie temperature of 28.0 ± 0.2 K and a saturation value of B = 25.7 ± 0.1 T at 4.2 K. The results are discussed briefly in terms of the bonding in these compounds and the magnetic exchange interactions in Eu_2RuH_6.

THERE is considerable interest in the preparation and physical properties of ternary hydrides formed from alkaline- or rare-earths and 3*d* or 4*d* transition elements, primarily because of their potential use as hydrogen storage materials.[1-3] Mössbauer spectroscopy can give detailed information about such systems, as shown recently by Buschow and co-workers, who used the 21.53 keV † resonance in ^{151}Eu to study the mechanisms of hydrogen absorption in the intermetallic compounds $EuRh_2$,[4] EuPd,[4] $EuNi_5$,[5] and $EuMg_2$.[5] In this paper we present the results of ^{99}Ru Mössbauer measurements at 4.2 K on the ternary hydrides M_2RuH_6 (M = Ca, Sr, Eu, or Yb), together with ^{151}Eu Mossbauer spectra from 4.2 K to room temperature on Eu_2RuH_6.

The preparation, structure, and properties of these compounds have been described by Moyer and co-workers.[6-8] In particular a neutron diffraction study on Sr_2RuD_6 revealed that the ruthenium is six-co-ordinate with respect to deuterium. Magnetic susceptibility measurements down to *ca.* 80 K were consistent with the presence of low-spin Ru^{II} (t_{2g}^{6}) and Eu^{II} ($S = \frac{7}{2}$) with an estimated moment of 7.82 B.M. (calc. 7.94 B.M.). The compound Eu_2RuH_6 was shown to obey a Curie–Weiss law above 85 K, with $\theta = 43$ K suggestive of ferromagnetic interactions, but measurements were not carried down to the predicted Curie temperature.

The present study was designed to obtain independent evidence concerning the various oxidation states, and to provide greater insight into the chemical bonding and magnetic interactions in these compounds. The measurements on Eu_2RuH_6 are particularly noteworthy in this respect, as they constitute the first example of the combined use of ^{151}Eu and ^{99}Ru Mössbauer measurements on one and the same sample.

EXPERIMENTAL

Samples of all the ternary hydrides were kindly supplied by Professor R. O. Moyer, jun. They were received in sealed tubes and transferred unopened into an argon-filled glove box, where they were made up into Mossbauer absorbers (*ca.* 400 mg cm^{-2} of compound for the ^{99}Ru measurements and *ca.* 50 mg cm^{-2} for the ^{151}Eu measurements).

The ^{99}Ru Mossbauer spectra were recorded using established techniques[9] and a nominal 5 mCi source of ^{99}Rh in a ruthenium metal matrix, prepared at A.E.R.E., Harwell. Both source and absorber were cooled to 4.2 K. The ^{151}Eu spectra were recorded using a nominal 300 mCi source of ^{151}Sm as samarium fluoride, supplied by the Radiochemical Centre, Amersham.

After the Mössbauer spectra had been recorded, powder *X*-ray diffraction measurements were made on a Philips powder diffractometer, using nickel-filtered Cu-K_α radiation, to check the purity of the samples. The patterns revealed small amounts of unreacted ruthenium metal in all the samples, plus a trace of impurity (probably EuO) in the sample of Eu_2RuH_6. However, the lattice parameters for all four samples were in excellent agreement with the published values.[6-8]

RESULTS AND DISCUSSION

The ^{99}Ru Mössbauer spectra at 4.2 K for the four ternary hydrides M_2RuH_6 (M = Ca, Sr, Eu, or Yb) consisted of a single line at -0.29 mm s^{-1} with a weak shoulder at zero velocity due to an impurity of Ru metal. A representative spectrum of Eu_2RuH_6 is shown in Figure 1, the very small percentage absorption (*ca.* 0.25%) being due to the low recoil-free fraction for the 90 keV transition in the hydride phase. The presence of ruthenium as an impurity is to be expected from the method of preparation and was confirmed from *X*-ray powder patterns; however, the area ratio of the two peaks (1 : 3.33) does not reflect the relative amounts of Ru and Eu_2RuH_6 because of the very different recoil-free fractions in the metal and the hydride phase.

TABLE 1

^{99}Ru Mossbauer parameters at 4.2 K for the hydrides M_2RuH_6

Phase	Chemical isomer shift [a] δ/mm s^{-1}	Linewidth Γ/mm s^{-1}	$\chi^2(d)$ [b]
Ca_2RuH_6	$-0.27(2)$ [c]	0.53(6)	259(240)
Sr_2RuH_6	$-0.30(1)$	0.26(1)	237(239)
Eu_2RuH_6	$-0.29(1)$	0.36(3)	308(240)
Yb_2RuH_6	$-0.27(1)$	0.26(3)	219(239)

[a] Relative to ruthenium metal. [b] d = Degrees of freedom. [c] Figures in parentheses are standard deviations in last significant figure.

The ^{99}Ru Mössbauer parameters for the four ternary hydrides are given in Table 1. The chemical isomer shifts are almost identical for all four compounds; they

---

† Throughout this paper: 1 eV ≈ 1.60 × 10^{-19} J; 1 B.M. = 9.274 × 10^{-24} A m^2.

fall well within the range for ruthenium(II) compounds (—0.93 to —0.08 mm s^{-1})[10] and outside the range of values for ruthenium(III) complexes (—0.84 to —0.50 mm s^{-1}). The absence of quadrupole splitting, implicit in the analysis and confirmed by the sharpness of the curve-fitted linewidths, is also consistent with the presence of Ru^{II} in an octahedral environment. It is not possible to be more specific about the electronic configuration of ruthenium in these phases. Indeed, from recent work of Danon and co-workers[11] it appears that the observed chemical isomer shift of —0.29 mm s^{-1} is consistent with an actual charge on the ruthenium of anywhere between zero and +2.

Further convincing, though indirect evidence for the presence of ruthenium(II) in these phases comes from the ^{151}Eu Mossbauer spectra of Eu_2RuH_6 shown in Figure 2. At room temperature the spectrum comprises two sharp singlets with chemical isomer shifts (Table 2) of —11.14 and 0.82 mm s^{-1}, which can be assigned unequivocally to Eu^{II} and Eu^{III}, respectively.[12] The former is assigned to the hydride while the latter is thought to arise from an Eu_2O_3 impurity. Although the areas under the two peaks are in the ratio 8.4 : 1, there is evidence (see later) that the recoil-free fraction of the hydride is very low at room temperature and that the actual amount of Eu_2O_3 present is very small indeed. Certainly there is no evidence in the *X*-ray powder diffraction pattern for its presence in appreciable quantities. Although it is generally established[13] that the hydrogen in rare-earth hydrides is anionic, the observation that both europium and ruthenium are divalent in Eu_2RuH_6 constitutes independent evidence in favour of a hydridic model of the bonding in this particular compound.

At 4.2 K the Eu^{II} resonance clearly exhibits magnetic hyperfine splitting. This is consistent with the magnetic susceptibility data,[7] which suggested that Eu_2RuH_6 is ferromagnetic with a Curie temperature below 77 K. Recent unpublished measurements by Moyer[14] show a pronounced increase in the magnetization of Eu_2RuH_6 at *ca.* 30 K, which strongly suggests the onset of ferromagnetic ordering at this temperature. However, unlike that of most ferromagnets, the magnetization of Eu_2RuH_6 appears to go through a maximum at about 20 K, decreasing thereafter down to 8 K, the lowest temperature of measurement. An analogous behaviour has been observed by Buschow *et al.*[4] for the ternary hydride $EuRh_2H_x$, in which the magnetization processes at low temperature are thought to be governed strongly by cluster effects. In order to obtain an independent check on the magnetic ordering temperature and the apparently anomalous magnetization behaviour in Eu_2RuH_6, we studied the temperature dependence of its ^{151}Eu Mössbauer spectrum at intervals of 5 K over the temperature range 10—60 K.

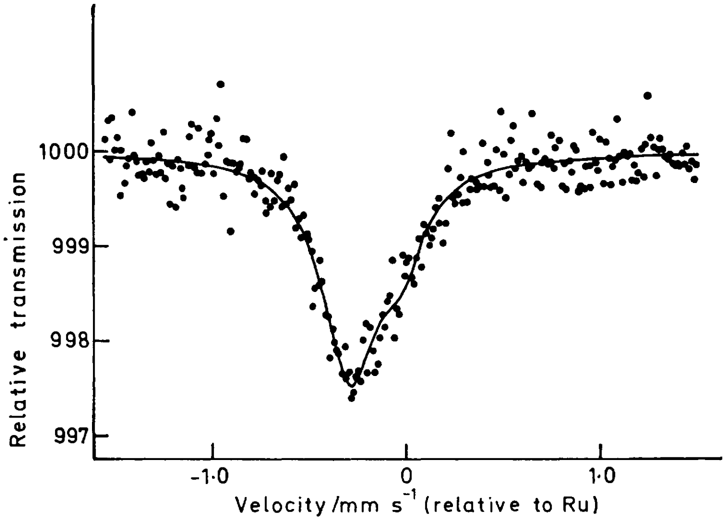

FIGURE 1 ^{99}Ru Mossbauer spectrum at 4.2 K of the ternary hydride Eu_2RuH_6. The shoulder at zero velocity arises from a trace of elemental ruthenium whose recoil-free fraction is considerably greater than that of the hydride

As the temperature is raised from 4.2 K there is a gradual collapse of the magnetic hyperfine pattern, and the behaviour over the temperature range 4.2—25.0 K appears relatively straightforward. However, from 35.0 to 60.0 K it is quite clear that the spectra cannot be interpreted satisfactorily on the basis of a single magnetic hyperfine pattern: as the magnetically split spectrum of Eu_2RuH_6 collapses, a second hyperfine pattern is revealed which arises from a phase with an ordering temperature higher than that of the hydride. The presence of EuO was suspected from the powder *X*-ray diffraction measurements, and visual comparison of the experimental spectra with data extracted from a paper by Wickman and Catalano[15] on the temperature dependence of the magnetic hyperfine field in EuO leaves little doubt that this second impurity is indeed EuO.

The computed Mössbauer parameters for Eu_2RuH_6 are given in Table 2 and the values for the magnetic flux density at the europium nucleus are plotted against temperature in Figure 3. Plotted on the same axes is the $S = \frac{7}{2}$ Brillouin function, calculated for a Néel temperature of 28 K and a saturation value for the magnetic flux density of 25.7 T. The agreement between the experimental data and the theoretical curve is excellent, and it is significant that there is no indication, whatsoever, of any anomalous behaviour in the region of 20 K similar to that displayed by the magnetization. Additional magnetization measurements on different preparations should reveal whether the anomalous behaviour reflects some unusual property intrinsic to Eu_2RuH_6 itself, or whether it is simply an artefact associated with the presence of the EuO and Eu_2O_3

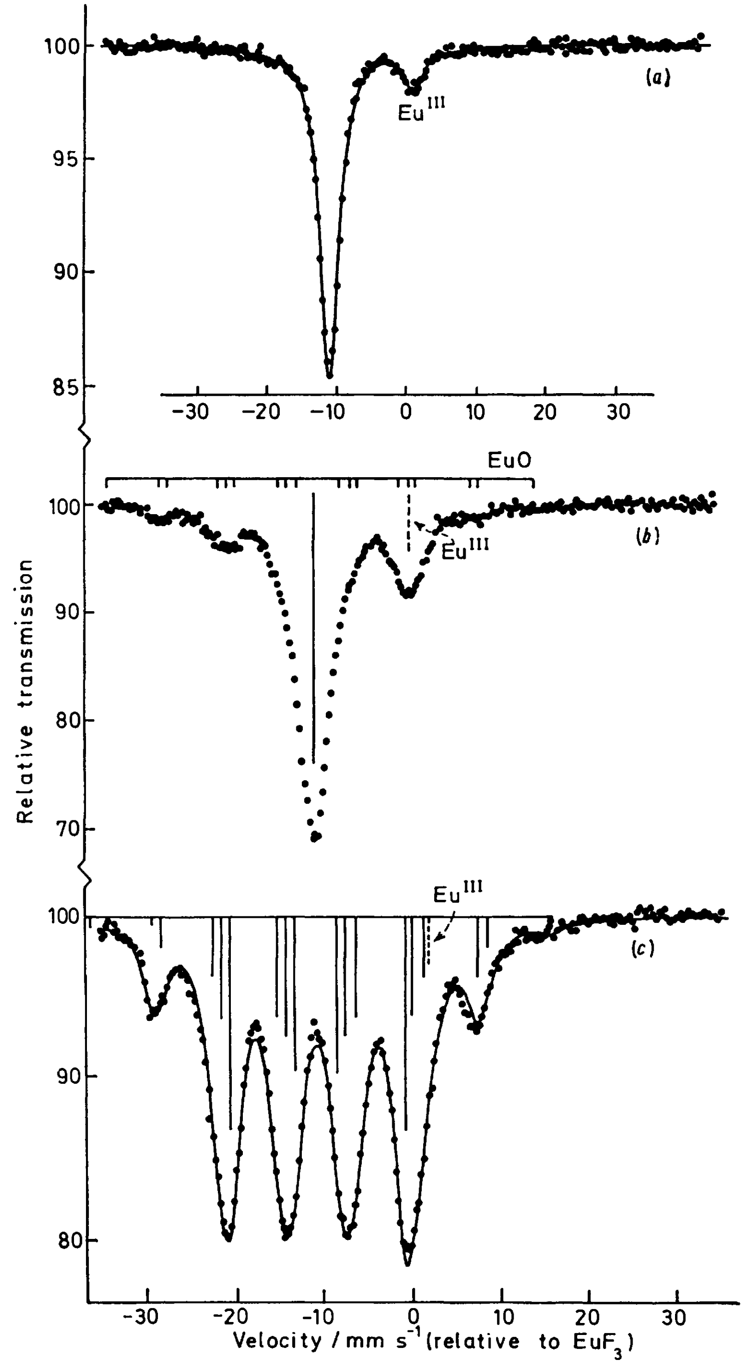

FIGURE 2 ^{151}Eu Mossbauer spectra of Eu_2RuH_6 at (*a*) room temperature, (*b*) 30.0 K, and (*c*) 4.2 K. The Eu^{III} component present in all three spectra probably arises from a trace of Eu_2O_3. The stick diagram in (*c*) represents the computed positions and intensities of the 18 components of the magnetically split pattern resulting from the $I_g = \frac{5}{2}$ to $I_e = \frac{7}{2}$ transition in Eu_2RuH_6. In (*b*) the predicted magnetic hyperfine pattern for EuO at 30 K is seen to correspond precisely with the magnetically split Eu^{II} impurity pattern. Note the dramatic reduction in the recoil-free fraction of the hydride phase above the Curie point ($T_c = 28.0$ K), relative to that of the EuO and Eu_2O_3 impurity phases impurities. It is interesting to note that the Curie temperature ($T_c = 28$ K) for Eu_2RuH_6 determined from the Mössbauer study coincides with the pronounced increase in the magnetization, but differs significantly from the Curie–Weiss constant ($\theta = 43$ K) deduced from the magnetic susceptibility measurements.[7]

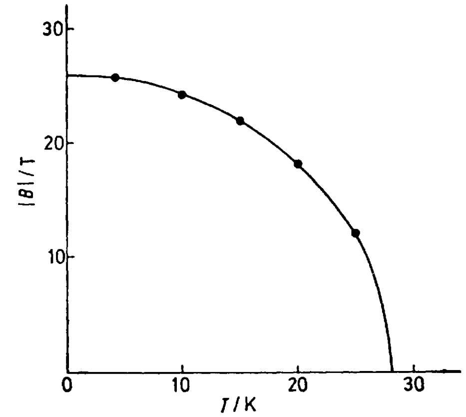

FIGURE 3 Temperature dependence of the magnetic flux density at the ^{151}Eu nucleus in Eu_2RuH_6. The solid curve represents the $S = \frac{7}{2}$ Brillouin function calculated for a Curie temperature of 28 K and a magnetic flux density at saturation of $B = 25.7$ T

At the lower temperatures (4.2—25.0 K) the proportion of the resonance area attributable to EuO is no more than *ca.* 5% of the total, and the actual amount of EuO present could well be less than this, depending on the relative recoil-free fractions of Eu_2RuH_6 and EuO.

TABLE 2

^{151}Eu Mössbauer parameters for Eu_2RuH_6

Temperature T/K	Chemical isomer shift [a,b] δ/mm s^{-1}	Magnetic flux density [c] B/T	Linewidth Γ/mm s^{-1}	$\chi^2(d)$ [d]
4.2	−11.36	25.7	2.76	891(238)
10.0	−11.36	24.2	2.82	844(238)
15.0	−11.39	21.9	3.03	462(238)
20.0	−11.38	18.2	3.31	1 315(238)
25.0	−11.46	12.1	3.83	639(238)
30.0—60.0 [e]	*ca.* −11.5	*ca.* 0	*ca.* 4.0	
298 [f]	−11.14	0	3.27	393(239)

[a] Relative to EuF_3 at room temperature. Note that the $^{151}SmF_3$ source was at 4.2 K except in the room temperature run. [b] Approximate errors ±0.05 mm s^{-1}. [c] Approximate errors ±0.5 T. The ratio of the nuclear magnetic moments used in the analysis was $\mu_e : \mu_g = 0.7465 : 1$ with $\mu_g = 3.4649\ \mu_N$ ($\equiv \mu_g = 1.521$ mm s^{-1} T^{-1}). [d] The rather high values for χ^2 reflect the fact that the weak EuO impurity peaks have not been included in the analysis, d = degrees of freedom. [e] Spectra were recorded at intervals of 5.0 K in this temperature range, but were not computed. [f] Both source and absorber were at room temperature.

Above the Curie temperature of Eu_2RuH_6 ($T_c = 28$ K) there is a dramatic increase in the relative area under the EuO resonance, as illustrated by the spectrum at $T = 30$ K in Figure 2. This results from a sudden decrease in the recoil-free fraction of Eu_2RuH_6 at the Curie point, and it seems likely that magnetostrictive phenomena similar to those proposed for EuH_2 [16] are also operative in Eu_2RuH_6.

The dominant contribution to the ^{151}Eu magnetic hyperfine field (B) in europium(II) compounds is thought to arise from core polarization of the inner s shells by the $4f$ electrons, and is estimated to be *ca.* −34 T.[12] However, polarization of conduction or valence s electrons can give rise to contributions of opposite sign, which vary in magnitude from compound to compound. As Eu_2RuH_6 is known [7] to be a semiconductor, the absolute value of $B = 25.7 \pm 0.5$ T observed at 4.2 K for the magnetic flux density at the ^{151}Eu nucleus in this compound suggests an admixture of 6s electron density into the Eu^{II} configuration from covalency effects (*i.e.* $4f^75s^26s^x$). This is also consistent with the observed value of $\delta = -11.36$ mm s^{-1} for the chemical isomer shift, which indicates an increase in s electron density at the europium nucleus relative to that in an ionic $4f^6$ material such as EuF_2 for which $\delta = -13.58$ mm s^{-1}. However, it is not obvious whether the 6s admixture into the Eu^{II} configuration results primarily from covalent interactions with other Eu^{II} ions, with the Ru^{II} ions, or with the hydride ions, and for this reason we do not attempt to estimate a value for the 6s occupancy.

Finally, it is interesting to note that there is no transferred magnetic hyperfine field at the diamagnetic ruthenium(II) ion in Eu_2RuH_6 at 4.2 K, despite the fact that the material is ferromagnetically ordered. The result strongly suggests that the ruthenium ions are not involved in the exchange mechanisms leading to cooperative long-range order, even though the Eu–Ru separation (327.6 pm) is less than the Eu–Eu separation (378.3 pm). Neither can the exchange take place *via* conduction electrons as Eu_2RuH_6 is a semiconductor with a negligible carrier concentration at 4.2 K. It therefore seems likely that the coupling mechanisms leading to ferromagnetism in Eu_2RuH_6 are similar to those operating in EuH_2, which is also a non-conducting ferromagnet ($T_c = 24$ K).[17] It is generally accepted that the Eu–Eu separation in EuH_2 (363—387 pm) is too great to allow direct exchange *via* the overlap of $4f$ orbitals on adjacent Eu^{II} ions,[13,16] and the same will apply to Eu_2RuH_6. It is probable that the dominant interaction in both hydrides involves indirect cation–cation exchange *via* overlapping $5d_{t_{2g}}$ orbitals on adjacent Eu^{II} ions, coupled with intraionic $4f$–$5d$ exchange, though an indirect transfer mechanism involving the hydrogen cannot be ruled out.[16]

We thank Professor R. O. Moyer (Trinity College, Connecticut) for making samples of the four compounds available and for helpful discussions, the S.R.C. for an equipment grant, and the Spanish Government for a postdoctoral fellowship (to I. F.).

[9/1488 *Received*, 19*th September*, 1979]

REFERENCES

[1] R. O. Moyer, jun., and R. Lindsay, *J. Solid State Chem.*, submitted for publication, and refs. therein.

[2] H. H. van Mal, K. H. J. Buschow, and A. R. Miedema, *J. Less-Common Metals*, 1976, **49**, 473.

[3] J. H. N. van Vucht, F. A. Kuijpers, and H. C. A. M. Bruning, *Philips Res. Rep.*, 1970, **25**, 133.

[4] K. H. J. Buschow, R. L. Cohen, and K. W. West, *J. Appl. Phys.*, 1977, **48**, 5289.

[5] F. W. Oliver, K. W. West, R. L. Cohen, and K. H. J. Buschow, *J. Phys. (F)*, 1978, **8**, 701.

[6] R. O. Moyer, jun., C. Stanitski, J. Tanaka, M. I. Kay, and R. Kleinberg, *J. Solid State Chem.*, 1971, **3**, 541.

[7] J. S. Thompson, R. O. Moyer, jun., and R. Lindsay, *Inorg. Chem.*, 1975, **14**, 1866.

[8] R. Lindsay, R. O. Moyer, jun., J. S. Thompson, and D. Kuhn, *Inorg. Chem.*, 1976, **15**, 3050.

[9] T. C. Gibb, R. Greatrex, and N. N. Greenwood, *J. Solid State Chem.*, 1980, **31**, 153.

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

[11] S. K. Lie, D. Guenzburger, and J. Danon, *Chem. Phys. Letters*, 1978, **55**, 347.

[12] C. M. P. Barton and N. N. Greenwood, in 'Mössbauer Effect Data Index (1973 Literature),' eds. J. G. Stevens and V. S. Stevens, Plenum, New York, 1975, p. 395.

[13] A. H. Zaheer, W. G. Bos, P. J. Ouseph, and S. L. Ruby, *J. Inorg. Nuclear Chem.*, 1976, **38**, 103.

[14] R. O. Moyer, jun., personal communication.

[15] H. H. Wickman and E. Catalano, *J. Appl. Phys.*, 1968, **39**, 1248.

[16] A. Mustachi, *J. Phys. Chem. Solids*, 1974, **35**, 1447, and refs. therein.

[17] R. L. Zanowick and W. E. Wallace, *Phys. Rev.*, 1962, **126**, 537.