^{151}Eu MÖSSBAUER STUDIES OF Eu$_2$IrH$_5$

ZBIGNIEW M. STADNIK*

Department of Physical Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen (The Netherlands)

RALPH O. MOYER, Jr.

Department of Chemistry, Trinity College, Hartford, CT 06106 (U.S.A.)

Summary

^{151}Eu Mössbauer measurements of the ternary hydride Eu$_2$IrH$_5$ in the temperature range 4.2 - 300 K are reported. It is shown that the europium ions are divalent and that the hyperfine magnetic field H_{hf} at the ^{151}Eu nuclei follows a $J = 7/2$ Brillouin function with $T_C = 19.9$ (0.4) K and $H_{hf}(T = 0) = 243.7$ (5.3) kOe. The exchange mechanism causing ferromagnetism in Eu$_2$IrH$_5$ is probably the same as that in EuH$_2$.

1. Introduction

Hydrides have been intensively studied in the last few years, but until recently most of the investigations have dealt with binary metallic hydrides [1, 2]. Now there is much interest in ternary hydrides [3]. Among the different experimental techniques used, Mössbauer spectroscopy is useful since many hydrides contain elements for which there exists a suitable Mössbauer isotope. The application of Mössbauer spectroscopy to investigations of hydrides has been recently discussed in reviews by Wagner and Wortmann [4], Cohen [5] and Shenoy *et al.* [6]. In particular, the ^{151}Eu Mössbauer technique, which is used in the present paper, was used to study the europium dihydride EuH$_2$ [7, 8], the hydrides of alloys Eu$_{0.025}$Pd$_{0.975}$ [9], EuPd [10], EuRh$_2$ [10, 11], EuMg$_2$ [12], EuNi$_5$ [12], (La$_{0.9}$Eu$_{0.1}$)Ni$_{4.6}$Mn$_{0.4}$ [13, 14] and the ternary hydride Eu$_2$RuH$_6$ [15].

The ternary hydride Eu$_2$IrH$_5$ was studied by Moyer and Lindsay [16] using X-ray diffraction, electrical resistivity and magnetometric measurements. In particular, they showed that above 140 K the temperature dependence of the susceptibility could be fitted with the Curie–Weiss law.

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*On leave from the Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Cracow, Poland. Present address: Department of Physics, University of Manitoba, Winnipeg, Manitoba R3T 2N2, Canada.

The paramagnetic Curie temperature θ derived from the fit was 18 K, suggesting ferromagnetic ordering. This was confirmed by their low temperature data which showed a sharp increase in magnetization at T_C = 20 K. The value of the Curie constant was consistent with the europium ions being divalent. Resistivity data indicated semiconductor behavior of the compound.

The present Mössbauer study was performed to obtain independent evidence concerning the magnetic interactions in Eu_2IrH_5 and the oxidation state of the europium ions.

2. Experimental details

A polycrystalline sample of Eu_2IrH_5 was prepared by mixing EuH_2 and iridium powders in a 2:1 mole ratio and heating the mixture at 973 K in a hydrogen atmosphere. The reaction is

$$2EuH_2(s) + Ir(s) + \frac{1}{2} H_2(g) \longrightarrow Eu_2IrH_5(s)$$
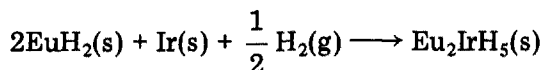
Further details of the sample preparation are given elsewhere [16]. Elemental analysis of Eu_2IrH_5 confirmed its chemical composition. An X-ray diffraction pattern showed a pure ternary phase and a trace of impurity in the form of EuH_2.

A Mössbauer absorber of thickness 27.5 mg cm^{-2} was prepared by mixing some sample with boron nitride and pressing the mixture into a lucite container, which was then covered with aluminum foil. Mössbauer measurements were made in the temperature range 4.2 - 300 K using the 21.53 keV transition in ^{151}Eu. Spectra were recorded with a conventional constant-acceleration spectrometer using a $^{151}Sm(SmF_3)$ source kept at 4.2 or 300 K. The multichannel analyzer was operated in the time mode. Calibration was by a Michelson interferometer with an He-Ne laser. A symmetric sawtooth reference signal produced two mirror Mössbauer spectra, which were later folded and fitted by a computer program [17]. γ rays were detected by an Xe-CO_2-filled proportional counter. The source and absorber temperature measurement and stabilization are accurate to within 0.5% at all temperatures.

3. Results and discussion

A typical Mössbauer spectrum in the paramagnetic region is shown in Fig. 1. It comprises two singlets with isomer shifts of -10.933 (0.007) and 0.645 (0.010) mm s^{-1} (Table 1), which are characteristic of Eu^{2+} and Eu^{3+} ions respectively [18]. The former can be assigned to the ternary hydride and some EuH_2 impurity, whereas the latter arises from an Eu_2O_3 impurity. The Mössbauer absorber was prepared in an atmosphere of ambient air. Under this condition EuH_2 is unstable and consequently partially oxidized
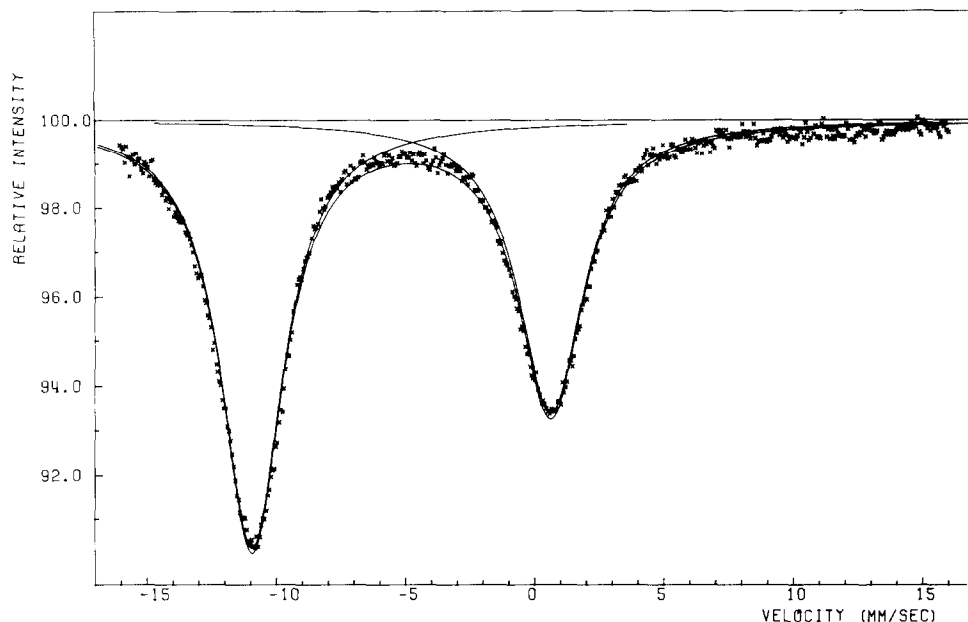
Fig. 1. ^{151}Eu Mössbauer spectrum of Eu_2IrH_5 with both source and absorber at 300.3 K.

TABLE 1

^{151}Eu Mössbauer parameters of the Eu_2IrH_5 sample in the paramagnetic region

T_a (K)	Mössbauer parameters for Eu^{2+}		Mössbauer parameters for Eu^{3+}	
	δ (mm s^{-1})	Γ (mm s^{-1})	δ (mm s^{-1})	Γ (mm s^{-1})
300.3[a]	−10.933 (0.007)	2.912 (0.022)	0.645 (0.010)	3.064 (0.035)
78.3[a]	−10.895 (0.008)	3.102 (0.026)	0.713 (0.011)	3.211 (0.037)
20.0[b]	−11.172 (0.011)	3.870 (0.034)	0.592 (0.012)	3.532 (0.036)

T_a, absorber temperature; δ, isomer shift relative to the ^{151}Sm(SmF$_3$) source; Γ, the full linewidth at half-maximum absorption.
[a]Source at 300 K.
[b]Source at 4.2 K.

forming Eu_2O_3. The actual amount of Eu_2O_3 present in the sample is smaller than that suggested by the area ratio of the lines, since Eu_2O_3 has a comparatively large recoil-free fraction [15]. As a result of the large difference in isomer shifts of Eu^{2+} and Eu^{3+} ions [18], the presence of Eu_2O_3 in the sample does not affect the Mössbauer parameters of the ternary hydride.

The temperature dependence of the isomer shift (Table 1) is caused by the second-order Doppler effect [19]. The decrease in the full linewidth at half-maximum absorption with increasing temperature (Table 1) is due to both spin relaxation effects [20, 21] and a temperature dependence of the effective absorber thickness [19].
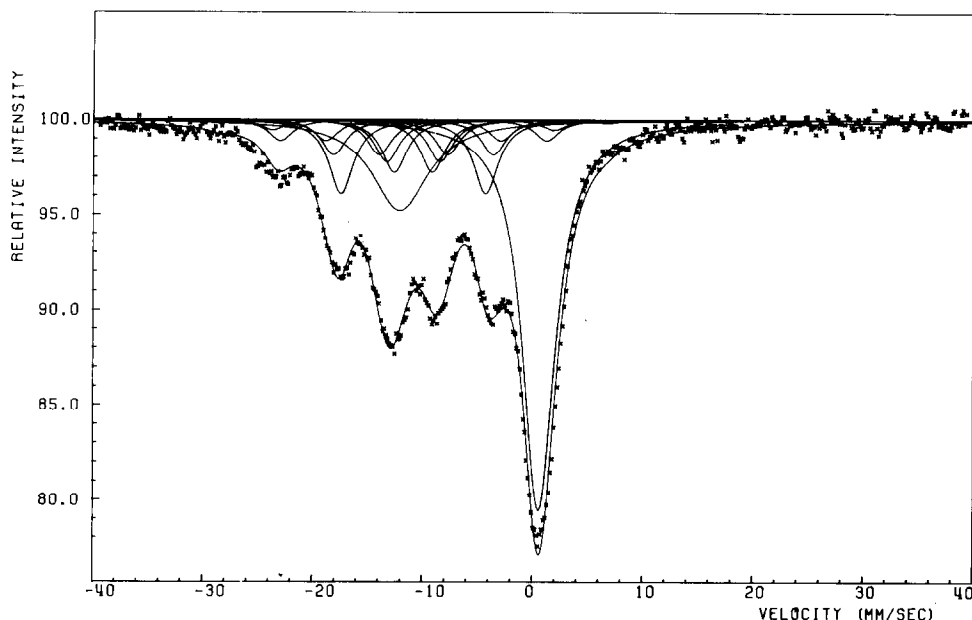
Fig. 2. ^{151}Eu Mössbauer spectrum of Eu_2IrH_5 at 14.0 K (the source was at 4.2 K).

Below the ordering temperature, the spectra consist of the following three subspectra (Fig. 2): an 18-line Zeeman pattern centered at -10.88 (0.03) mm s^{-1} corresponding to Eu^{2+} ions in Eu_2IrH_5; a single very broad line at -11.91 (0.06) mm s^{-1} due to Eu^{2+} ions in EuH_2; a single line at 0.59 (0.02) mm s^{-1} corresponding to Eu^{3+} ions in Eu_2O_3. The Curie temperature of EuH_2 is 16.2 K [7], and therefore its Mössbauer spectrum close to T_C can be well approximated by a single line.

Values of the hyperfine magnetic fields H_{hf} in Eu_2IrH_5 were derived from spectra taken at different temperatures assuming the following: the ratio μ_e/μ_g of the nuclear magnetic moment of the excited state to the ground state is 0.7465 and $\mu_g = 3.465\mu_N$ [22]. The results are shown in Fig. 3 together with the fit to a $J = 7/2$ Brillouin function. The parameters derived from the fit are the saturation hyperfine magnetic field $H_{hf}(0) = 243.7$ (5.3) kOe and the Curie temperature $T_C = 19.9$ (0.4) K.

The value of the isomer shift $\delta = -10.88$ mm s^{-1} lies between that of highly ionic EuF_2 (-13.58 mm s^{-1} [18]) and that of europium metal (-7.8 mm s^{-1} [18]). This means that the s electron density at ^{151}Eu nuclei in Eu_2IrH_5 is larger than that in EuF_2 and smaller than that in europium metal. This is in accordance with previous Mössbauer studies [5 - 15] which showed that the value of the electron density at the ^{151}Eu nuclei in hydrides is reduced from that in metallic systems. In divalent europium compounds the electronic configuration can be represented by $(4f)^7(5s)^2(6s)^x$ [23], with $x = 0$ for EuH_2. The value δ of -10.88 mm s^{-1} for Eu_2IrH_5 indicates some admixture of the 6s electron density caused by covalency effects. This is confirmed by the fact that the hyperfine magnetic field $H_{hf}(0) = 243.7$ kOe

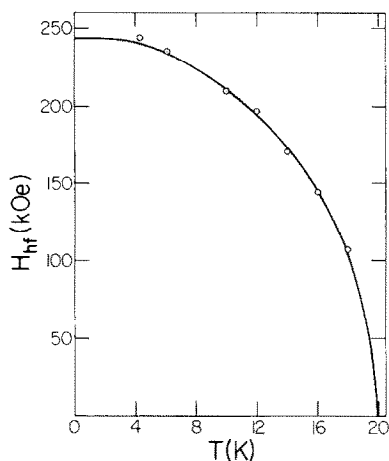Fig. 3. Temperature dependence of the hyperfine magnetic field H_{hf} at the [151]Eu nuclei in Eu$_2$IrH$_5$: ———, fit to a $J = 7/2$ Brillouin function.

in Eu$_2$IrH$_5$ is smaller than the absolute value of the core polarization contribution to $H_{hf}(0)$ of -340 kOe for Eu^{2+} ions in insulators [24]. The difference of about $+100$ kOe is due to a contribution to H_{hf} arising from the polarization of conduction or valence s electrons, a phenomenon expected since Eu$_2$IrH$_5$ is a semiconductor [16].

The results of [151]Eu Mössbauer investigations of hydrided intermetallics showed [5, 10, 12] that the values of δ and H_{hf} were close to those for EuH$_2$, which was interpreted as evidence of the importance of the Eu—H bond. Our values of δ and H_{hf} for Eu$_2$IrH$_5$, as well as those for Eu$_2$RuH$_6$ [15], are also close to those for EuH$_2$ [7]. This result is also noteworthy because the different preparations used (direct chemical synthesis for Eu$_2$IrH$_5$ [16] and Eu$_2$RuH$_6$ [15] and hydriding for other intermetallics [5 - 14]) might be expected to result in different hyperfine interactions.

The value T_C of 19.9 (0.4) K determined from the temperature dependence of H_{hf} is in excellent agreement with the value of 20 K found by Moyer and Lindsay [16]. For Eu$_2$RuH$_6$, $T_C = 28.0$ (0.2) K [15]. A comparison of T_C values for Eu$_2$IrH$_5$ and Eu$_2$RuH$_6$ with those of hydrided intermetallics (ref. 10, Table 1) shows a general constancy, as with the values of δ and H_{hf}. This constancy of T_C also demonstrates that the Eu—H bond is most important in determining the physical behavior of different hydrides.

The exchange mechanism leading to the magnetic ordering in hydrides is not well understood. It is believed that in Eu^{2+} hydrides the Eu–Eu separation (3.63 - 3.87 Å for EuH$_2$ [8]) is too large to allow direct exchange via the overlap of 4f orbitals on adjacent Eu^{2+} ions. This is probably also true for Eu$_2$IrH$_5$ hydride, for which the Eu–Eu distance is 3.790 Å. The exchange mechanism in Eu$_2$IrH$_5$ is probably similar to that in EuH$_2$ [7, 8], *i.e.* it arises either from the indirect cation–cation exchange via overlapping 5d (t$_{2g}$) orbitals on adjacent Eu^{2+} ions, which are coupled via intra-atomic 4f–5d exchange [8], or from the indirect routing of exchange via H$^-$ ions [7]. The

Eu–Ir distance in Eu_2IrH_5 of 3.282 Å is much smaller than the Eu–Eu distance. Thus it is probable that the iridium ions also participate in exchange. This can be tested with [193]Ir Mössbauer measurements which are planned for the future.

Acknowledgment

References

1 G. Alefeld and J. Völkl (eds.), *Hydrogen in Metals I, Top. Appl. Phys., 28* (1978).
   G. Alefeld and J. Völkl (eds.), *Hydrogen in Metals II, Top. Appl. Phys., 29* (1978).
2 G. G. Libowitz and A. J. Maeland, in K. A. Gschneidner, Jr., and L. Eyring (eds.), *Handbook on the Physics and Chemistry of Rare Earths*, Vol. 3, North-Holland, Amsterdam, 1979, p. 299.
3 K. H. J. Buschow, P. C. P. Bouten and A. R. Miedema, *Rep. Prog. Phys., 45* (1982) 937.
4 F. E. Wagner and G. Wortmann, in G. Alefeld and J. Völkl (eds.), *Hydrogen in Metals I, Top. Appl. Phys., 28* (1978) 131.
5 R. L. Cohen, *J. Phys. (Paris), Colloq. C1, 41* (1980) 333.
6 G. K. Shenoy, B. D. Dunlap, P. J. Viccaro and D. Niarchos, *Hydrogen Storage Materials, Adv. Chem. Ser. 194* (1981) 501.
7 A. Mustachi, *J. Phys. Chem. Solids, 35* (1974) 1447.
8 A. H. Zaheer, W. G. Bos, P. J. Ouseph and S. L. Ruby, *J. Inorg. Nucl. Chem., 38* (1976) 103.
9 M. Meyer, J. M. Friedt, L. Iannarella and J. Danon, *Solid State Commun., 17* (1975) 585.
10 K. H. J. Buschow, R. L. Cohen and K. W. West, *J. Appl. Phys., 48* (1977) 5289.
11 R. L. Cohen, K. W. West and K. H. J. Buschow, *Solid State Commun., 25* (1978) 293.
12 F. W. Oliver, K. W. West, R. L. Cohen and K. H. J. Buschow, *J. Phys. F, 8* (1978) 701.
13 R. L. Cohen, K. W. West and J. H. Wernick, *J. Less-Common Met., 70* (1980) 229.
14 R. L. Cohen, K. W. West and J. H. Wernick, *J. Less-Common Met., 73* (1980) 273.
15 I. Fernandez, R. Greatrex and N. N. Greenwood, *J. Chem. Soc., Dalton Trans.,* (1980) 918.
16 R. O. Moyer, Jr., and R. Lindsay, *J. Less-Common Met., 70* (1980) P57.
17 G. H. M. Calis, *Ph.D. Thesis*, University of Nijmegen, Nijmegen, 1981.
18 E. R. Bauminger, G. M. Kalvius and I. Nowik, in G. K. Shenoy and F. E. Wagner (eds.), *Mössbauer Isomer Shifts*, North-Holland, Amsterdam, 1978, p. 661.
19 P. Gütlich, R. Link and A. Trautwein, Mössbauer spectroscopy and transition metal chemistry, in *Inorganic Chemistry Concepts*, Vol. 3, Springer, Berlin, 1978.
20 G. Groll, *Z. Phys., 243* (1971) 60.
21 G. Ya. Selyutin, *Phys. Lett. A, 62* (1977) 350.
22 J. G. Stevens, in J. W. Robinson (ed.), *Handbook of Spectroscopy*, Vol. III, Chemical Rubber Co., Boca Raton, FL, 1981, p. 464.
23 H. H. Wickman, I. Nowik, J. H. Wernick, D. A. Shirley and R. B. Frankel, *J. Appl. Phys., 37* (1966) 1246.
24 J. M. Baker and F. I. B. Williams, *Proc. R. Soc. London, Ser. A, 267* (1962) 283.