Mössbauer Spectroscopic Study of the Gadolinium–Hydrogen System

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A study has been carried out of the gadolinium–hydrogen system using ^{155}Gd sources (from ^{155}Eu) incorporated in SmF_3 and $SmPd_3$. Sources were held at 4.2 K and absorbers at various temperatures. Using the ' single-line ' Sm(^{155}Eu)Pd_3 source, isomer shifts (in mm s^{-1}) relative to GdF_3 are: Gd, -0.71 ± 0.02; GdH_2, -0.10 ± 0.02; GdH_3, -0.11 ± 0.02 at 4.2 K. The hyperfine magnetic field in GdH_2 is -306 ± 30 kG (for the metal it is -382 ± 10 kG). GdH_3 is quadrupole split, $V_{zz} = (5.1 \pm 0.5) \times 10^{17}$ V cm^{-2}. Isomer-shift data are qualitatively in accord with the anionic model of hydride formation. Electron density at the gadolinium nucleus decreases most markedly with initial addition of hydrogen and little, if any, on going from GdH_2 to GdH_3. The reverse is observed for the hyperfine magnetic field at the gadolinium nucleus. Electric and magnetic effects are discussed in relation to other relevant chemical and physical properties of the system.

HYDROGEN reacts exothermally with the lanthanoids giving non-stoicheiometric hydride systems with hydrogen to metal ratios extending up to 3 except for europium and possibly ytterbium. Two models have been proposed to explain their properties and the nature of the bonds between the metal and the hydrogen.[1] One is based on the postulate that the hydrogen exists in the lattice in protonic form, the other that it is in anionic form. Evidence purporting to support one or other of these forms has been obtained and the matter is therefore still not resolved.

Mössbauer spectroscopy would seem to be a useful technique to apply to this problem. Only two publications [2,3] have appeared relating to structural aspects of such hydride systems. Both were carried out using ^{161}Dy as the Mössbauer source, the former at room temperature, the latter at low temperatures. In the work described here ^{155}Gd sources were used at 4.2 K with absorbers at several temperatures. Results are presented and discussed in relation to the protonic and anionic models and to the earlier Mössbauer spectroscopic studies where relevant.

EXPERIMENTAL

Hydride Preparation.—Gadolinium metal foil (0.25 mm in thickness and containing <0.1% of other lanthanoids) was obtained from Metals Research Ltd., Royston, England. Each sample of composition $GdH_{1.4}$ to $GdH_{2.1}$ was prepared by treating the metal foil (1.5 g), cut in small pieces, at 500 °C with the required amount of hydrogen. To ensure a homogeneous product the hydride preparation was held at 500 °C for 12 h and then rapidly cooled. To GdH_2 thus prepared, hydrogen pressures of *ca.* 1 atm and a reaction temperature of 200 °C, maintained for 36 h, followed by slow cooling to room temperature, gave GdH_3.

Absorber Preparation.—The absorbers for the spectral measurements were prepared in an argon-filled dry-box. For the preliminary measurements about half the hydride sample was transferred to a mortar and ground to a paste with addition of a few drops of dry Nujol. The paste was spread evenly over a circular depression (25 mm diam.) in aluminium foil (0.0024 cm thick) and then encapsulated by covering with foil and sealing the edges with Durafix. Such capsules were found to exclude the atmosphere efficiently for a period of several weeks during which time they were twice cycled between room temperature and 4 K. In the later work using the $SmPd_3$ source matrix (see below) the powdered sample was sandwiched between two metal plates separated by an O-ring seal.

Mössbauer Spectra.—One of the two sources consisted of 10 mCi ^{155}Eu incorporated in a SmF_3 matrix; it was supplied by the Radiochemical Centre Ltd., Amersham, England. The other was prepared from $^{154}SmPd_3$ by irradiation in a neutron flux to produce ^{155}Eu.

The Sm(^{155}Eu)F_3 source was driven in the constant acceleration mode as described previously.[4] The counter consisted of a thin Na(Tl)I crystal scintillator; it was set to detect the 86.5 keV γ-ray from ^{155}Gd. Harwell 2000 series electronic units were used to amplify, process, and select signals from the counter. A Laben 512 channel analyser used in the multiscalar mode served to collect the information. Both source and absorber were immersed in liquid helium and spectra were obtained over periods of 50—70 h depending on the volume of the initial liquid helium charge (generally 2 l).

The arrangement of cryogenic equipment was slightly different when the $^{154}SmPd_3$ source was used. A metal cryostat containing the source and absorber was surrounded by a superconducting magnet and the whole unit immersed in liquid helium contained in a glass dewar. The temperature of the source and the absorber could be varied and measured independently. The magnet produced uniform fields up to 60 kG along the direction of absorption of the γ-rays and zero field at the source. The 87.5 keV γ-rays were detected by a lithium-drifted germanium counter which was not affected by the small stray magnetic fields from the magnet.

The magnetic hyperfine spectrum of ^{57}Fe in enriched iron metal, for which splittings are known accurately,[5] was used to calibrate and frequently check the velocity scale of the spectrometers.

RESULTS AND DISCUSSION

In the preliminary investigations using the Sm(^{155}Eu)F_3 source and the Na(Tl)I detector the 86.5 keV and, unavoidably, the 105 keV gamma rays from ^{155}Gd were detected in the counting arrangement described. Both are known [6,7] to undergo nuclear resonance absorption.

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[1] G. G. Libowitz, ' The Solid-State Chemistry of Binary Metal Hydrides,' Benjamin Inc., New York, 1965.

[2] T. P. Abeles, W. G. Bos, and P. J. Ouseph, *J. Phys. Chem. Solids*, 1969, **30**, 2159.

[3] J. Hess, E. R. Bauminger, A. Mustachi, I. Nowik, and S. Ofer, *Phys. Letters*, 1971, **37A**, 185.

[4] S. J. Lyle and A. D. Witts, *J.C.S. Dalton*, 1975, 185.

[5] R. S. Preston, S. S. Hanna, and J. Herberle, *Phys. Rev.*, 1962, **128**, 2207.

[6] H. Blumberg, B. Person, and M. Bent, *Phys. Rev.*, 1969, **170**, 1076.

[7] H. Prange, *Z. Phys.*, 1968, **212**, 415.

Following the work of Cashion *et al.*[8] and checks carried out by the authors, the latter is not considered to contribute appreciably to the spectra obtained in the present studies. This source, nevertheless, does not emit a single 'line.' A pseudo-doublet is obtained from an electric quadrupole interaction giving rise, in theory, to five lines; the two 'components' are separated by *ca.* 1.3 mm s^{-1}. Spectra obtained are, therefore, only likely to yield relatively limited information. Mössbauer spectra of all the hydride samples and also of gadolinium metal obtained using it consist of a broad absorption line. Spectral widths measured at half maximum height are recorded in Table 1. They may be compared with the natural width, $2\tau = 0.53$ mm s^{-1}.[9]

The results of measurements made with GdH_2 and GdH_3 absorbers using the $Sm(^{155}Eu)Pd_3$ source are collected in Table 2. This is a 'single-line' source, of width 0.55 ± 0.01 mm s^{-1}, and as can be seen it provides considerably more precise data on isomer shifts; these are consistent, where comparison is possible, with the more extensive survey of the hydride system set out in Table 1. Bowden *et al.*[10] have shown that the strengths of the magnetic and quadrupole interactions on the ground state of ^{155}Gd are comparable in Gd metal and, if the directions of quantization of the magnetic and quadrupole interactions do not coincide, considerable admixture of Zeeman levels results. In a polycrystalline sample this makes it impossible to derive meaningful hyperfine parameters. In order to overcome this complication a 2.8 atomic % Gd–Tm alloy was used. The easy direction of magnetisation is along the *c*-axis (the direction of the electric field gradient V_{zz}) and so no off-diagonal elements arise in the combined magnetic and quadrupole Hamiltonian. This reduces the number of lines in the Mössbauer spectrum from 24 to 12. The magnetic field quoted in Table 2 has been corrected for the slight reduction in the average spin per atom which results when a gadolinium atom is replaced by a thulium atom and which, in turn, reduces the hyperfine value to that measured (Zmora *et al.*[11]). V_{zz} In h.c.p. metals is very sensitive to the $c:a$ ratio and the difference in V_{zz} between the dilute alloy and the pure metal[12] is a reflection of this fact.

TABLE 1

Isomer shifts (in mm s^{-1}) relative to GdF_3 and spectral widths (in mm s^{-1}) at half-maximum height from spectra obtained at 4.2 K with the $Sm(^{155}Eu)F_3$ source

	Isomer shift	Width
Gd metal	-0.6 ± 0.1	4.9
$GdH_{1.4}$	-0.1 ± 0.1	4.8
$GdH_{1.5}$	-0.1 ± 0.1	4.8
$GdH_{2.1}$	0.0 ± 0.1	4.6
$GdH_{3.0}$	0.0 ± 0.1	4.5

It is of interest to relate the results to known electronic and magnetic properties of the gadolinium–hydrogen system. The ground-state electronic configuration of gadolinium can be written as $(Xe)4f^7 5d^1 6s^2$ and that of gadolinium(III) as $(Xe)4f^7$; $\Delta R/R$, where $\Delta R = R_{ex} - R$ the difference between the excited (86.5 keV level) and the ground-state nuclear charge radii of ^{155}Gd, is reported[7] to be negative. Hence an increase in electron density at the nucleus in the absorber will give rise to a negative isomer shift. The observed negative shift (Table 1) for the metal relative to GdF_3 indicates that the increased nuclear screening to be expected from the $5d^1$ electron is more than compensated by the addition of the $6s^2$ electrons which are responsible for the net increase in electron density at the nucleus.

In the protonic model, it is postulated[1,13] that hydrogen, on entering the metallic lattice, 'donates' its electron to the conduction band which assumes a $5d$–$6s$ character. Addition of hydrogen beyond MH_2 causes a splitting of this band, the lower (in energy) component assuming $5d$ character can accommodate 6 electrons per metal atom. Evidence to support this band-splitting theory has come, for example, from nuclear spin lattice relaxation times for yttrium in YH_2; they indicate that there is little *s* character at the Fermi energy level.[2,14] On this interpretation, GdH_3 could be expected to have a full $5d$-like conduction band. A positive isomer shift for the gadolinium nucleus in this electronic environment relative to GdF_3 might be expected. The extent of the expected shift depends on the screening capability of the $5d$-type conduction electrons. The fact that $GdH_{3.0}$ has a negative shift relative to GdF_3 is then not in accord with the protonic model unless the electrons in the now filled conduction band have negligible shielding effect on electron density at the nucleus. Isomer shifts to be expected on the basis of this model for hydrides of intermediate composition would depend on the relative degrees of $6s$ and $5d$ character in the conduction band. As definitive data on this point are lacking it is fruitless to speculate on the trend to be expected in isomer shifts relative to those found experimentally (Table 1) for the intermediates.

From the anionic model, the trihydride has the same electronic configuration as the trifluoride and an isomer shift of zero is to be expected for a pure ionic solid. However, whilst the isomer shift of GdH_3 is much closer to that of GdF_3 than Gd metal, it is still negative relative to the trifluoride (14% shift from GdF_3 compared to the metal). There must be additional *s*-electron density at the nucleus in GdH_3 relative to the completely ionic trifluoride. This could arise from partial covalent bonding with the hydride ions as suggested by Abeles *et al.*[2] in the dysprosium–hydrogen system. An alternative explanation would follow from the observation

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[8] J. D. Cashion, D. B. Prowse, and A. Vas, *J. Phys.* (*C*), 1973, **6**, 2611.

[9] A. Marelius, P. Sparrman, and T. Sundstrom in 'Hyperfine Structure and Nuclear Radiations,' eds. E. Mathias and D. A. Shirley, North Holland, Amsterdam, 1968, p. 1072.

[10] G. J. Bowden, J. W. Ross, and K. A. McEwen, Proceedings of the 18th Ampere Congress, to be published.

[11] H. Zmora, M. Blau, and S. Ofer, *Phys. Letters*, 1969, **28A**, 668.

[12] E. R. Bauminger, D. Froindlich, A. Mustahi, I. Nowik, S. Ofer, and S. Samuelov, *Phys. Letters*, 1969, **30B**, 531.

[13] G. G. Libowitz, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 837.

[14] D. S. Schreiber, *Phys. Rev.*, 1965, **137**, A860.

that the trihydride showed evidence of magnetic ordering at 1.3 K. This could lead to the conclusion that if this magnetic ordering was sustained by the RKKY interaction then conduction electrons are present since the trihydride may have been slightly hydrogen deficient (*cf.* EuH_2 [15]). Such a deficiency, estimated at <5%, would decrease the isomer shift relative to GdF_3. It must be borne in mind, however, that conditions are favourable for the observation of magnetic hyperfine splittings in paramagnetic lanthanide salts even though they are not magnetically ordered. The necessary condition is that the spin relaxation times between the various populated ionic states are longer than the reciprocal of the Larmor frequency characterising the magnetic hyperfine interactions.[16]

Isomer shifts to be expected for intermediate hydrides will again depend on the nature of the defect level conduction band proposed. From a simplistic stance, the anionic model would predict electronic configurations $(Xe)4f^75d^1$ and $(Xe)4f^75d^0$ for gadolinium in the di- and tri-hydride respectively and the slightly smaller negative shift for GdH_2 relative to GdH_3 (Table 2) due to the singly delocalised electron per metal atom in the dihydride defect band.

The relatively large change in isomer shift in going from the metal to $GdH_{1.4}$ compared to the change from $GdH_{1.4}$ to GdH_2 and GdH_2 to GdH_3 (Table 1) may well be significant in this respect.

The isomer-shift data presented here are generally in agreement with those of Cashion *et al.*[8] who did not, however, discuss their results in terms of metal–hydrogen interaction. They are also qualitatively in accord with the data of Abeles *et al.*[2] for the dysprosium hydrides, obtained using ^{161}Dy at room temperature. (Quantitative comparisons are invalid because of the temperature shift.)

It is known [1] that two phase changes occur in going from gadolinium metal to the trihydride. As the hydrogen to metal ratio increases the hexagonal close packed metal structure gradually gives way to a cubic phase stable in the GdH_2 region, in which hydrogen occupies the tetrahedral holes, and finally at GdH_3 to a hexagonal structure of the HoD_3 [17] type. Gadolinium metal is ferromagnetic ($T_C = 291$ K) [15] and GdH_2 is antiferromagnetic ($T_N = 21$ K) [15] at 4 K. Magnetic ordering has not been observed for the trihydrides down to 4 K.[1] However, as stated earlier, magnetic hyperfine effects were noticed in our sample at 1.3 K, and they are discussed above. No magnetic or conductivity data are available for this class of trihydride at very low temperatures.

For the dihydride, at a temperature of *ca.* 24 K, a single line resulted, width 0.93 mm s^{-1}, corresponding to a cubic structured paramagnet. At 4.2 K a hyperfine magnetic field of -306 ± 30 kG at the Gd nucleus was computed from the now antiferromagnetic dihydride spectrum. GdH_2 Is a metallic conductor and hence it can sustain the RKKY interaction. Hydriding the metal has reduced the strength of this interaction, reflected in a lower ordering temperature,[15] although the hyperfine field remains approximately constant within experimental error. According to the anionic model electrons are being removed from the gadolinium conduction band and localised about the hydrogen atoms lessening the RKKY interaction which could account for the above trend.

On the application of an external field, strength 60 kG, no change in the relative intensities of the Mössbauer lines was observed (see Table 2), indicating absence of polarised γ-rays. The gadolinium magnetic moments remain locked, hence the anisotropy field in GdH_2 at 4.2 K was greater than 60 kG.

The hexagonal trihydride produced an unresolved doublet spectrum at 4.2 K which was pure quadrupole split, estimated $V_{zz} = 2.8(3)$ mm s^{-1} or $5.1(5) \times 10^{17}$ V cm^{-1} (see Table 2).

TABLE 2

Data derived from Mössbauer spectra obtained with the $Sm(^{155}Eu)Pd_3$ source

Compound	Isomer shift mm s^{-1} [a]	Hyperfine field kG [c]	$V_{zz} \times 10^{-17}$ • V cm^{-2} [c]	Ref.
Gd metal	−0.71 (2) [b]	−382 (10)	2.67 (15)	10, P.W.
GdH_2	−0.10 (2)	−306 (30) [d]	N.S.†	P.W.‡
GdH_3	−0.11 (2)	0 [e]	5.1 (5)	P.W.

[a] Referred to GdF_3 as origin. [b] Error in last figure quoted as 3 times the root mean square deviation. [c] Measured at 4.2 K unless stated otherwise. [d] Application of a 60 kG external magnetic field did not produce a change in the relative intensities of the hyperfine lines, *i.e.* the anistropy field in GdH_2 is >60 kG. [e] A hyperfine magnetic field was observed at 1.3 K obtained by pumping on liquid helium.

* V_{zz} is the component of the electric field gradient tensor in the z direction. † N.S., no quadrupole splitting observed. ‡ P.W., present work.

V_{zz} may be expressed thus: [18]

$$V_{zz} = (1 - \gamma_\infty)eq_{zz}^{(\text{ion})} + (1 - R)eq_{zz}^{(4f)}$$

where
$$q_{zz}^{(\text{ion})} = \frac{-4A_2^0}{e^2} = \frac{-4V_2^0}{e^2(1 - \sigma_2)\langle r^2 \rangle}$$

and
$$\langle \nu | q_{zz}^{(4f)} | \nu \rangle = -\sum_k \langle \nu | \frac{3z_k^2 - r_k^2}{r_k^5} | \nu \rangle$$
$$= -\langle J \| \alpha \| J \rangle \langle r^{-3} \rangle \langle \nu | 3J_z^2 - J(J + 1) | \nu \rangle$$

γ_∞, R, and σ_2 are shielding parameters.

Referring to GdH_3, one may assume that the gadolinium is present as Gd^{3+} (ground state term $^8S_{7/2}$), so that $q_{zz}^{(4f)} = 0$, and using a Sternheimer antishielding factor of −61: [19]

$$A_2^0 = -2.1(2) \times 10^{15} \text{ V cm}^{-2}$$

However, theoretical computations of A_2^0 based on a point-charge model are not feasible at present for

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[15] W. E. Wallace, *Ber. Bunsengesellschaft Phys. Chem.*, 1972, **76**, 832.

[16] H. W. Wickman and G. K. Wertheim in ' Chemical Applications of Mössbauer Spectroscopy,' eds. V. I. Goldanskii and R. H. Herber, Academic Press, New York, 1968, ch. 11.

[17] M. Mansmann and W. E. Wallace, *J. Phys.*, 1964, **25**, 454.

[18] R. L. Mössbauer, *Rev. Mod. Phys.*, 1964, **36**, 362.

[19] R. P. Gupta and S. K. Sen, *Phys. Rev.* (*A*), 1973, **7**, 850.

GdH_3. This arises because only extrapolated values for the lattice constants and Gd–H separations are available and then only for the deuteriated system HoD_3 at room temperature.[17] Large errors (~10%) result in Qe/Qg [12] and there are problems in assigning a meaningful charge to the hydrogens surrounding the gadolinium nucleus. A comparison of A_2^0 (protonic) or A_2^0 (anionic) with the experimental value should prove instructive in elucidating the nature of hydrogen in gadolinium trihydride.

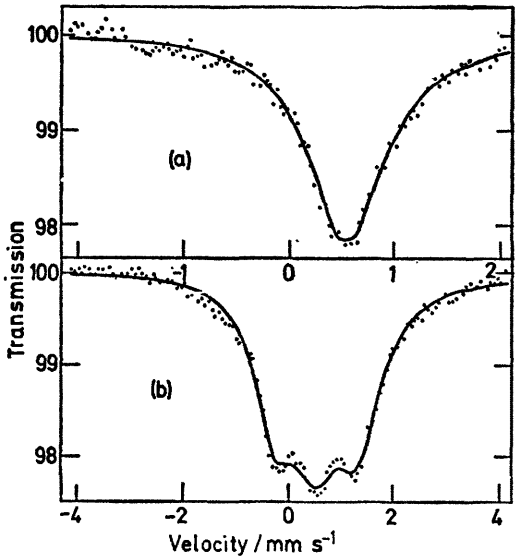

FIGURE 1 Mössbauer spectra of GdH_2 above (a; $T = 24$ K) and below (b; $T = 4.2$ K) the Néel point (21 K), using the $Sm(^{155}Eu)Pd_3$ source at 4.2 K

It is seen from the preceding discussion that our results are consistent with those predicted by the 'Anionic Model of Metal Hydrides.' In general, however, over a wide range of experimental data, the results are not consistent with a single model, be it anionic, protonic, or covalent. A non-rigid band approach has been discussed[20] in relation to this problem and may ultimately be of value when quantitatively developed.

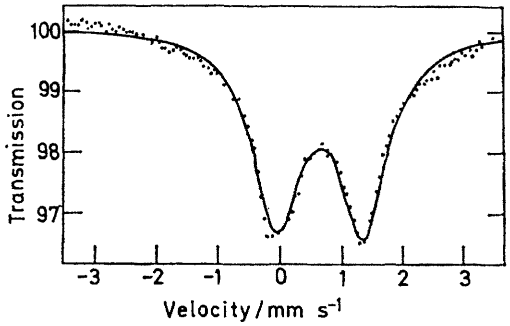

FIGURE 2 Mössbauer spectrum of GdH_3 obtained with the $Sm(^{155}Eu)Pd_3$ source. Both source and absorber were at 4.2K

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[20] A. C. Switendick, *Solid State Comm.*, 1970, **8**, 1463.