# The Gadolinium–Hydrogen System

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Isomer shifts have been measured above and below the Néel temperature (21 K) for the dihydride phase of the gadolinium–hydrogen system at different H : Gd ratios using a $^{155}$Gd source. No evidence has been obtained for a quadrupole contribution to the observed spectra. The hyperfine magnetic field at the gadolinium nucleus within the dihydride phase range $GdH_{1.8}$ to $GdH_{2.3}$ does not change significantly with change in hydrogen content. Differences in the hyperfine magnetic-field strengths for $GdH_2$ and other metal-like gadolinium compounds are attributed to neighbour effects and possibly a large covalent contribution by hydrogen to the hyperfine magnetic field at the gadolinium nucleus. A comparison is made between the experimentally determined electric-field gradient in $GdH_3$ and values obtained by calculation using a point-charge model; the results clearly point to the anionic character of the hydrogen.

GADOLINIUM takes up hydrogen to give a dihydride having a fluorite-type structure which exists within the hydrogen : gadolinium limits of 1.8—2.3 : 1. Further hydrogen uptake produces a transformation to a phase in which the gadolinium has a hexagonal lattice, the H : Gd limits for which are 2.85—3.0 : 1. The dihydride has an electrical conductivity like that of a metal while the trihydride behaves like a semiconductor. In a previous study,[1] Mössbauer spectroscopy was used to obtain information about the chemical state of the hydrogen and the gadolinium at several hydride compositions. In a further study, described here, Mössbauer spectral parameters were measured as a function of hydrogen concentration within the limits of the metallic dihydride phase. Particular attention was given to the effect of large deviations from stoicheiometry ($GdH_2$) on the electric-field gradient (e.f.g.) at the gadolinium site. Gadolinium dihydride undergoes a magnetic transition at 21 K. Earlier Mössbauer spectroscopic measurements by Cashion *et al.*[2] at liquid-helium temperatures were interpreted in terms of a small quadrupole effect mixed in with the magnetic hyperfine effect

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[1] S. J. Lyle, P. T. Walsh, A. D. Witts, and J. W. Ross, *J.C.S. Dalton*, 1975, 1406.

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

observed in hydrogen-deficient $GdH_2$. The quadrupole splitting was thought to disappear on removal of the hydrogen deficiency. Quadrupole splitting should be most readily discernible in spectral measurements made above the Néel temperature. Hence, the present work on the dihydrides was carried out below and just above this temperature.

In addition, experimentally determined values of the e.f.g. in semiconducting $GdH_3$ have been compared with point-charge calculations to provide evidence for the charge state of the hydrogen in this substance.

## EXPERIMENTAL

*Hydride Preparation and Characterisation.*—The source and quality of the gadolinium foil has already been described.[1] The preparative procedures used previously [1] were modified as set out here. Each sample of composition within the range $GdH_{1.8}$ to $GdH_{2.3}$ was prepared by treating the metal with hydrogen at 773 K until the appropriate uptake of hydrogen had been achieved. The temperature was then decreased to 623 K and the sample annealed for 12 h. It was then allowed to cool slowly to room temperature. To produce $GdH_3$, the hydrogen pressure above the dihydride was increased to *ca.* 1 atm,* the reaction temperature was kept at 523 K for 36 h, and finally the furnace and contents were cooled to ambient temperatures.

The composition of each sample was calculated from the volume of hydrogen taken up by the metal. As a check, the hydrogen pressure above the hydride was compared with the relevant pressure–composition isotherm.[3] *X*-Ray powder crystallography was used to verify that a sample was within the appropriate phase limits [3] before running a Mössbauer spectrum. The dihydride diffraction pattern did not have lines in it due to hexagonal close-packed gadolinium metal, and trihydride samples did not possess lines attributable to the cubic dihydride. The long annealing times, together with the diffraction data, were taken as adequate proof that only single-phase samples were analysed by Mössbauer spectroscopy.

*Absorber Preparation.*—The absorbers for the Mössbauer spectroscopy were prepared in an argon-filled dry-box. Approximately 200 mg of dihydride was sandwiched uniformly between two Perspex discs each of 0.5 in diameter and 0.03 in thick. The sandwich was enclosed in a copper cylinder fitted with aluminised Mylar windows at each end. The copper cylinder was constructed in two parts; after loading with the sample the parts were sealed together with Durafix adhesive. Even after 3 weeks in such a holder the trihydride, which is more sensitive to air and water vapour than dihydride preparations, gave an unchanged Mössbauer spectrum.

*X*-Ray diffraction measurements were performed on these sealed samples.

*Mössbauer Spectra.*—The single-line source consisted of *ca.* 10 mCi of $^{155}Eu$ incorporated into a $SmPd_3$ lattice. The 86.5 keV $\gamma$-ray from the $^{155}Gd$ daughter was detected using a thin Na(Tl)I crystal scintillator. The source was driven in the constant-acceleration mode in a spectrometer similar to that described previously except that a Brandenburg series 4000 multichannel analyser was used in the multiscalar mode to accumulate spectral information. The source temperature was maintained at 4.2 K and the absorber temperature varied at will in a low-temperature cryostat supplied by the Oxford Instrument Co. Ltd. The magnetic hyperfine spectrum of $^{57}Fe$ in enriched iron metal was used to calibrate the velocity scale of the spectrometer. Spectral data were curve-fitted using the constrained linear-regression procedure of Stone.[4] The Lorentzian components of spectra exhibiting magnetic and quadrupole interactions were constrained to have equal linewidths and their intensities to be in the ratio of their respective transition probabilities.

## RESULTS AND DISCUSSION

*The Dihydride System.*—The results of the measurements on the dihydrides are summarised in Table 1. It may be assumed that diffusion of hydrogen in the absorbers is negligible at these temperatures. Evidence for quadrupole splitting was not obtained in any of the samples. Thus it appears that the vacant tetrahedral or occupied octahedral sites in hydrogen-deficient or -excessive dihydrides respectively do not reduce the local symmetry sufficiently to produce measurable electric-field gradients at the gadolinium nucleus. The detection of such an e.f.g. is hindered by the $^{155}Gd$ having small ground and excited quadrupole moments.

TABLE 1

Summary of results derived from Mössbauer spectra of gadolinium dihydride preparations

| H : Gd | *T*/K | I.s./mm s$^{-1}$ | *H*/kG | Q.s./mm s$^{-1}$ |
|---|---|---|---|---|
| 1.88 | 24 | 0.58 (0.02) | | 0.0 |
| | 4 | 0.62 (0.02) | 303 (20) | |
| 1.93 | 24 | 0.56 (0.02) | | 0.0 |
| | 4 | 0.56 (0.02) | 301 (20) | |
| 2.25 | 24 | 0.59 (0.02) | | 0.0 |
| | 4 | 0.61 (0.02) | 300 (20) | |

I.s. = the isomer shift relative to the $Sm(^{155}Eu)Pd_3$ source, *H* = the hyperfine magnetic field at the gadolinium nucleus, and q.s. = the ground-state quadrupole splitting. Errors recorded in parentheses are twice the standard deviation of the mean.

If the vacancies are randomly distributed then, for the sample with the lowest hydrogen content, *ca.* 10% of the gadolinium will have a tetrahedral vacancy as a neighbour instead of hydrogen. An n.m.r. study [5] indicated that, in the isostructural lanthanum dihydride system, all the tetrahedral sites were full at H : La = 1.95 : 1 so that 2.5% were inaccessible presumably due to impurity. For positive deviations from stoicheiometry, with random occupancy of octahedral sites, for H : Gd = 2.25 : 1, *ca.* 25% of the gadolinium sites would have an octahedral hydrogen as a near neighbour, in addition to four tetrahedrally placed hydrogens.

For a short-range quadrupole interaction due to hydrogen deficiency or excess, relative to H : Gd =

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* Throughout this paper: 1 atm = 101 325 Pa; 1 G = $10^{-4}$ T.

[3] G. E. Sturdy and R. N. R. Mulford, *J. Amer. Chem. Soc.*, 1956, **78**, 1083.

[4] A. J. Stone, in G. M. Bancroft, A. G. Maddock, W. K. Ong, R. H. Prince, and A. J. Stone, *J. Chem. Soc.* (*A*), 1967, 1966 as an appendix to the paper.

[5] D. S. Schreiber and R. M. Cotts, *Phys. Rev.*, 1963, **131**, 1118.

2.0 : 1, two contributions to the overall Mössbauer spectrum might be expected assuming there are two kinds of symmetry available to the gadolinium nucleus. The screened potential due to a point defect in a metallic conductor is given by [6] equation (1) where $\rho$ is the

$$\phi(r) = \rho r^{-1}\mathrm{e}^{-Kr} \qquad (1)$$

charge on the defect in units of electronic charge, $r$ the distance between the central ion and the defect, and $K = (6\pi Ne^2/E_F)^{\frac{1}{2}}$ is a screening factor. Therefore, the electric-field gradient, $q$, is given by [7] (2) where $\gamma_\infty$ is an

$$q = (1 - \gamma_\infty)\rho(3Z^2 - r^2)[1 + Kr + (K^2r^2/3)]\mathrm{e}^{-Kr}/r^5 \qquad (2)$$

antishielding factor. Taking $\gamma_\infty = 60$,[8] the free-electron value of $K \simeq 2 \times 10^8$ cm$^{-1}$, $\rho = 1$, and the nearest-neighbour distance for a tetrahedral vacancy in an anionic lattice $r = (3^{\frac{1}{2}}/4)a_0$, a value $q = 0.93$ kV nm$^{-2}$ is obtained. This corresponds to a ground-state quadrupole splitting, q.s. $= \frac{1}{2}e^2qQ_g = 0.26$ mm s$^{-1}$. For an octahedral interstice occupied by a hydride, H$^-$, species at $r = \frac{1}{2}a_0$ a value $q = -0.58$ kV nm$^{-2}$ leading to q.s. $= 0.16$ mm s$^{-1}$ is obtained.

The value of q.s. thus calculated cannot give more than a rough approximation to the maximum local e.f.g. at the gadolinium nuclei, but the presence of small fractions of sites having such spectral splitting would be difficult to detect as was observed in practice. The quadrupole splitting observed by Cashion *et al.*[2] for non-stoicheiometric dihydride might then have been due to a two-phase sample containing both non-stoicheiometric dihydride and hydrogen-saturated gadolinium metal.

The decrease in the strength of the magnetic interaction as H : Gd increases from 0 to 3 : 1 has been explained using an anionic model; [9] conduction electrons are removed from the metal and become localised about the hydrogen thus suppressing the exchange interaction between electrons in the conduction band and the 4$f$ electrons (RKKY interaction). For ions having the $4f^7$ electron configuration there is no direct field from the 4$f$ electrons. The contributions to the total hyperfine magnetic field, $H$, arise from core polarisation, conduction-electron polarisation by the 4$f$ electrons, and neighbour effects.[10,11] $H$ in GdH$_2$ would therefore contain these terms, the first two of which are approximately constant for metallic-like gadolinium compounds.[11,12] Thus differences in $H$ between the dihydride and other metallic gadolinium compounds are largely due to neighbour effects. In this respect $H$ in GdH$_2$ is larger than that in GdAl$_2$ (−160 kG) [12] where the gadolinium is surrounded by diamagnetic neighbours and the Gd–Gd distances in both substances are similar. This enhancement may be due to a large covalent contribution by the hydride ion, H$^-$, to the unbalanced spin density at the gadolinium nucleus. On the available evidence the variation in H : Gd ratio within the dihydride-phase limits producing such a small change in conduction-electron density would not be expected to affect $H$.

*The Trihydride System.*—A comparison was made between the experimentally determined e.f.g. in gadolinium trihydride and values obtained by calculation using a point-charge model. A computer was programmed to calculate $q^1$ [equation (3)] and the quadrupole splitting [equation (4)] where $\rho_i$ is the

$$q^1 = \sum_i [\rho_i(3Z_i^2 - r_i^2)/r_i^5] \qquad (3)$$

$$\text{q.s.} = \tfrac{1}{2}e^2(1 - \gamma_\infty)q^1Q_g = \tfrac{1}{2}eV_{zz}Q_g \qquad (4)$$

charge on ion $i$, $Z_i$ the distance of ion $i$ from the central ion along the principal axis of the e.f.g., and $r_i$ is the separation between $i$ and the central ion. The program was checked by comparing $q^1$ obtained for gadolinium metal with the more sophisticated method of Das and Pomerantz.[13] The agreement between the convergence limits was within 3%. The relative positions of the ions in the GdH$_3$ lattice and extrapolated values of the lattice parameters were taken from the neutron-diffraction study of HoD$_3$ at 298 K by Mansmann and Wallace.[14] The principal axis of the e.f.g. is directed along the crystal $c$ axis. To ensure convergence the summation was performed over a sphere of radius equal to 10 lattice parameters ($a_0$ 6.46 Å). Points at distances greater than this contribute less than 0.5% to $q^1$.

The variation in $V_{zz}$ for GdH$_3$ with a hypothetical charge on the hydrogen is set out in Table 2. Magnetic-susceptibility measurements on GdH$_3$ suggest [15] that the gadolinium is present as Gd$^{3+}$. The values for $V_{zz}$ with $\rho_{Gd} = 3$, *i.e.* not compensated for the change in hydrogen charge, are obtained assuming that the electrons in the 5$d$–6$s$ band, which can accommodate six electrons per metal atom according to the protonic model,[16] do not contribute to $V_{zz}$. If the charge on the gadolinium ions is altered to compensate for the change in hydrogen charge the lower series of $V_{zz}$ values (Table 2) is obtained. The 'true' variation in $V_{zz}$ with hydrogen and gadolinium charges might then be expected to lie between the extremes represented by the two series in Table 2. However, the trend in both series remains the same; $V_{zz}$ is positive for anionic hydrogen and negative for 'protonic' hydrogen. The experimental results obtained from the trihydride sample and $V_{zz}$ calculated using a value of

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[6] N. F. Mott and H. Jones, 'The Theory of the Properties of Metals and Alloys,' Oxford University Press, 1936.

[7] M. H. Cohen and F. Reif, *Solid State Phys.*, 1957, **5**, 321.

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

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

[10] H. Zmora, M. Blau, and S. Ofer, *Phys. Letters*, 1969, **A28**, 668.

[11] B. Bleaney, in 'Magnetic Properties of Rare Earth Metals,' ed. R. J. Elliott, Plenum, London and New York, 1972, ch. 8.

[12] R. E. Gegenwarth, J. I. Budnick, and S. Skalski, *Phys. Rev. Letters*, 1967, **18**, 9.

[13] T. P. Das and M. Pomerantz, *Phys. Rev.*, 1961, **123**, 2070.

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

[15] W. E. Wallace, Y. Kubota, and R. L. Zanowick, *Adv. Chem. Ser.*, 1963, **39**, 122.

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

$Q_g = 1.59$ and fitting the spectrum taking[17] the ratio of the excited- and ground-state quadrupole moments $Q_e : Q_g$ as 0.12 : 1 are presented in Table 3. The values of $V_{zz}$ in Table 2 were calculated using a monopole lattice. An estimate of the dipole contribution to $V_{zz}$ was made using a summation program since the $H^-$ ion is readily polarised. However, the contribution to $V_{zz}$ from a lattice of dipoles at the hydrogen sites was negligible compared to the monopole contribution. The inherent inadequacy of the point-charge model, especially for a species such as $H^-$, excludes the expectation of close agreement between calculated and experimentally derived $V_{zz}$. However, the results presented in Tables 2 and 3 clearly point to the anionic nature of the hydrogen in $GdH_3$.

TABLE 2

The component of the electric-field-gradient tensor in the $z$ direction, $V_{zz}$, calculated for different electron charges on the hydrogen, $\rho_H$, and gadolinium, $\rho_{Gd}$, in $GdH_3$

| $\rho_H$ (electron units) | −1.0 | −0.5 | 0.0 | 1.0 |
|---|---|---|---|---|
| $V_{zz}$/kV nm$^{-2}$ ($\rho_{Gd} = 3$) | 4.20 | 0.27 | −3.66 | −11.52 |
| ($\rho_{Gd} = -3\rho_H$) | 4.20 | 2.10 | 0.00 | −4.20 |

TABLE 3

Spectroscopic data for $GdH_3$, and $V_{zz}$ derived from them

| $T$/K | I.s.*/mm s$^{-1}$ | Q.s./mm s$^{-1}$ | $V_{zz}$/kV nm$^{-2}$ |
|---|---|---|---|
| 4 | 0.49 | 1.49 | 5.42 |

* Relative to Sm($^{155}$Eu)$Pd_3$.

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