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MÖSSBAUER EFFECT OBSERVATION OF DIVALENT GADOLINIUM

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Résumé. — L'absorption résonnante des rayons γ de 86,5 keV de ^{155}Gd a été utilisée pour détecter le gadolinium divalent dans $\text{CaF}_2 : \text{Gd}$. Le déplacement isomérique mesuré entre Gd^{2+} et Gd^{3+} est $+ (0,35 \pm 0,09) \text{ mm s}^{-1}$, ce qui confirme la structure électronique $4f^7 5d^1$ de Gd^{2+} . On déduit la valeur $\Delta \langle r^2 \rangle = - (8,2 \pm 2,1) \times 10^{-3} \text{ fm}^2$ pour la transition de 86,5 keV. Les éclatements mesurés pour le gadolinium dans l'état divalent sont beaucoup plus élevés que pour le gadolinium trivalent.

Abstract. — Resonant absorption of the 86.5 keV gamma rays from ^{155}Gd has been used to detect divalent gadolinium in $\text{CaF}_2 : \text{Gd}$. The isomer shift between Gd^{2+} and Gd^{3+} was measured to be $+ (0.35 \pm 0.09) \text{ mm s}^{-1}$ confirming that the electron configuration of Gd^{2+} is $4f^7 5d^1$. The value of $\Delta \langle r^2 \rangle$ for the 86.5 keV transition was deduced to be $- (8.2 \pm 2.1) \times 10^{-3} \text{ fm}^2$. The measured splittings for gadolinium in the divalent state were found to be considerably larger than for trivalent gadolinium.

1. Introduction. — The isomer shift observed in a Mössbauer experiment is the electric monopole interaction between the nucleus and the electrons. The parameters involved in its interpretation are the change in the mean-square nuclear charge radius, $\Delta \langle r^2 \rangle$, between the ground and excited states and the difference in the electron density at the nucleus in the source and absorber $\Delta |\psi(0)|^2$. The determination of $\Delta \langle r^2 \rangle$ is usually carried out by measuring the isomer shift between ionic compounds of two different valence states of the nuclide concerned and then using a self-consistent-field calculation to estimate $|\psi(0)|^2$ for the two free ion configurations.

However gadolinium is probably the most difficult of the rare earths to obtain in a valence state other than the usual trivalent one and this has hampered determinations of $\Delta \langle r^2 \rangle$ values for gadolinium isotopes. In order to try and improve the current estimate of $\Delta \langle r^2 \rangle$ for the principal Mössbauer transition in gadolinium, the 86.5 keV gamma ray in ^{155}Gd , and determine it on a consistent basis with the other rare earths, we have attempted to produce divalent gadolinium. Another factor of interest in the experiment was the likelihood that the electron configuration of Gd^{2+} would be $4f^7 5d^1$ instead of the conventional $4f^8$, although this unfortunately reduces the size of the isomer shift and hence lowers the accuracy of the $\Delta \langle r^2 \rangle$ determination.

2. Sample preparation. — CaF_2 was chosen as the host since it is a light cubic material containing a cation of the correct valency and ionic radius and has already been used successfully for producing divalent rare earths for optical and Mössbauer experiments. Samples were prepared from CaF_2 and GdF_3 by mechanically mixing the correct proportions of finely ground powder, pressing and then sintering at 1300°C for 24 h. Samples were prepared using 11 at. % and 1 at. % Gd and cut into thicknesses of 8 mm and 15 mm respectively.

Three methods were used to try and enhance the ratio of $\text{Gd}^{2+}/\text{Gd}^{3+}$. The first two methods were solid state electrolysis and irradiation in the direct beam of a 2 kW x-ray set for 24 h, neither of which produced any detectable change in the Mössbauer absorption spectrum. The third method [1] was to heat the samples in calcium vapour for 3 h at approximately 600°C and the results of this will be described in the next section.

The single line source used for all experiments was SmPd containing approximately 4 at. % Sm. The sample was irradiated for 7 days at $3 \times 10^{13} \text{ neutrons cm}^{-2} \text{ s}^{-1}$ to produce a 1 mCi source via the $^{154}\text{Sm}(n, \gamma)$ reaction.

3. Results. — All measurements were taken using a conventional constant acceleration drive mounted vertically in a helium cryostat with both the source and absorber at 4.2 K. The spectra were recorded on a 400 channel analyzer.

Measurements on the samples containing 11 % Gd

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in CaF_2 all gave symmetrical spectra. However considerable differences were observed between samples and two spectra obtained are shown in figure 1a and b. We

FIG. 1. — Mössbauer absorption spectra of two different samples of 11 % trivalent gadolinium in calcium fluoride.

were unable to determine systematically the causes for such a large change in the spectra which are apparently due to small changes in the chemical preparation.

All the spectra can be explained by quadrupole splitting alone and no evidence was found for a site of cubic symmetry at the centre of the spectrum. Fourteen different lines were observed with the parameters being given in Table I. We would tentatively assign the

TABLE I
 Gd^{3+} in CaF_2

Line Positions	Isomer Shift	Splitting
+ 0.13(10) + 1.03(10)	0.58	0.9
− 0.27(10) + 1.43(10)	0.58	1.7
− 0.77(1) + 1.95(1)	0.59	2.72
− 1.31(5) + 2.47(5)	0.58	3.78
− 1.55(10) + 2.71(10)	0.58	4.3
− 2.03(10) + 3.03(10)	0.50	5.1
− 2.55(10) + 3.60(10)	0.52	6.1
+ 0.58(3)	0.58	0 (**)

Gd^{2+} in CaF_2

Line Positions	Isomer Shift	Splitting
+ 0.93(7)	0.93	0
− 0.97(3) + 2.80(3)	0.92	3.77
− 2.77(10) + 4.63(10)	0.93	7.4
− 4.60(10) + 6.46(10)	0.93	11.1
− 6.50(15) + 8.50(15)	1.0	15.0
− 8.1(2) + 9.9(2)	0.9	18.0

All measurements are in units of mm s^{-1} .

The figure in brackets indicates the error in the last digit.

(**) See text.

dominant spectrum in figure 1a with a splitting of $(2.72 \pm 0.02) \text{ mm s}^{-1}$ to a Gd^{3+} ion accompanied by a charge compensating F^- at the next vacant interstitial site in the simple cubic fluorine sublattice as observed by Baker *et al.* [2].

From Table I we would estimate that the isomer shift of $\text{CaF}_2:\text{Gd}^{3+}$ is $+(0.58 \pm 0.02) \text{ mm s}^{-1}$ with respect to our SmPd source. This can be compared with the isomer shift for GdF_3 and $\text{Gd}_2(\text{SO}_4)_3$ of 0.66 – 0.67 mm s^{-1} [3] and the typical range of Gd^{3+} isomer shifts in insulators of 0.45 – 0.67 mm s^{-1} .

As mentioned in section 2, x-irradiation and solid state electrolysis did not produce any discernable change in the spectrum. However heating in calcium vapour produced a small peak at $+(0.95 \pm 0.08) \text{ mm s}^{-1}$ barely observable against the dominant Gd^{3+} spectra. It is to be remembered that in trying to observe this peak there is also a contribution from the photoelectric effect interference term which tends to make the central region asymmetrical in the opposite direction.

We interpret this single peak as being due to a Gd^{2+} ion which is now in a site of cubic symmetry due to the diffusing away of the charge compensating fluorine interstitial. However it seemed reasonable to assume that in the cases where gadolinium atoms were close together they would be more stable and hence resist reduction to Gd^{2+} . Further experiments were therefore carried out on samples of 1 % Gd in CaF_2 , again heated in calcium vapour.

The spectrum produced was now definitely asymmetrical with an appreciable contribution from both divalent and trivalent gadolinium up to a maximum of approximately 20 % divalent. One of these spectra is shown in figure 2 and again slightly different spectra were produced by different samples. Separation of these spectra was difficult but was achieved mainly

FIG. 2. — Mössbauer absorption spectrum of 1 % gadolinium in calcium fluoride containing both divalent and trivalent gadolinium. The line intensity shown dotted could not be resolved in this spectrum between the two proper line positions shown on either side. The asymmetry in the outer peaks is due to non-linearity near the drive turnaround.

by subtraction of spectra taken before and after calcium treatment, helped by the fact that different samples emphasized different lines. However all the spectra were fitted to the same lines and these parameters are also given in Table I. The mean isomer shift for $\text{CaF}_2 : \text{Gd}^{2+}$ was estimated to be $+ (0.93 \pm 0.07) \text{ mm s}^{-1}$ with respect to SmPd .

Heating the sample in calcium vapour also sometimes resulted in the production of a Gd^{3+} spectrum which is unsplit or at most has a quadrupole splitting of less than a linewidth (0.8 mm s^{-1}). If it is really an unsplit line due to Gd^{3+} in a site of cubic symmetry then the probable mechanism would seem to be reduction to Gd^{2+} and the subsequent diffusing away of the charge compensating F^- ion during the calcium treatment, followed by a later reversion to Gd^{3+} . This is supported by our frequent observation that the spectrum appeared to change during running (although such conclusions are easy to draw with inadequate statistics) and subsequent running produced a different spectrum. However with a typical running time of 1-2 weeks there does seem a possibility that radiation-induced defects were in fact annealing out the divalent spectrum.

4. Discussion. — The current literature value (4) of $\Delta \langle r^2 \rangle$ for ^{155}Gd is $-(6 - 10) \times 10^{-3} \text{ fm}^2$ and this would indicate an isomer shift of

$$\begin{aligned}\delta(4f^8 - 4f^7) &\approx 1.4 \text{ mm s}^{-1} \\ \delta(4f^7 5d^1 - 4f^7) &\approx 0.3 \text{ mm s}^{-1}\end{aligned}$$

for the two possible configurations of divalent gadolinium.

It is therefore clear that the Gd^{2+} is in the configuration $4f^7 5d^1$ as suggested by McClure and Kiss [5] from their optical experiments.

As part of a detailed comparison of isomer shifts in different rare earths [6] we have carried out relativistic Hartree-Fock calculations of $|\psi(0)|^2$ for these free ion configurations. Using these results in conjunction with the measurement

$$\begin{aligned}\delta(\text{CaF}_2 : \text{Gd}^{2+}) - \delta(\text{CaF}_2 : \text{Gd}^{3+}) &= \\ &= + (0.35 \pm 0.09) \text{ mm s}^{-1}\end{aligned}$$

gives us the value $\Delta \langle r^2 \rangle = -(8.2 \pm 2.1) \times 10^{-3} \text{ fm}^2$. This is in good agreement with the value

$$- 8.7 \times 10^{-3} \text{ fm}^2$$

obtained in [6] from other measurements.

The measured hyperfine splittings of the divalent spectra are a factor of four larger than those for gadolinium in the trivalent state. The largest quadrupole splitting previously reported is 5.4 mm s^{-1} in monoclinic Gd_2O_3 [3]. Larger hyperfine splittings for Gd^{2+} are to be expected because the outer electronic shell no longer possesses the symmetry of the half-filled $4f^7$ configuration.

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