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^{155}Gd Mössbauer spectra of Gd^{3+} in borate glasses

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Abstract. Lithium–borate glasses containing 0.1–10 mol% Gd_2O_3 have been studied by ^{155}Gd Mössbauer spectroscopy. Isomer shifts near 0.6 mm s^{-1} , independent of the Gd concentration, are in the range typical of ionic Gd compounds. The spectra are very well described by a distribution of quadrupole splittings corresponding to a random distribution of ligand coordinations. Additional temperature-independent broadening of the resonance lines is ascribed to effects of spin–spin relaxation of Gd moments.

1. Introduction

Nuclear techniques such as NMR or Mössbauer spectroscopy have been employed extensively in studies of glasses [1]. Both techniques use nuclei as local probes. Modifications of nuclear energy levels resulting from effects of fields and potentials due to electric charges and magnetic moments in the local environment yield information on the structure and on site symmetries at an atomic scale as well as on magnetic interactions in the case of glasses containing magnetic ions.

In contrast to the large variety of nuclei used in NMR studies, most investigations by Mössbauer spectroscopy have been performed with ^{57}Fe or with ^{119}Sn [1]. Although many rare-earth nuclei are suitable probes for Mössbauer spectroscopy, only ^{151}Eu seems to have been used in a very limited number of Mössbauer studies of ionic glasses [2, 3].

The present work, reporting results derived from Mössbauer spectra of ^{155}Gd in $\text{Li}_2\text{O}-\text{B}_2\text{O}_3$ glasses, was stimulated by the results of an earlier investigation of similar borate glasses containing EuO by ^{151}Eu Mössbauer spectroscopy [3]. A quantitative analysis of the ^{151}Eu spectra could not be achieved. However, simulation of ^{151}Eu Mössbauer spectra employing several models had yielded the surprising result that spectra calculated with a model involving valence contributions to the electric field gradient were in better agreement with the experimental data than those calculated with other models. The quadrupole splitting of the nuclear ground state of ^{155}Gd is generally better resolved than that of ^{151}Eu levels. Hence, Mössbauer spectra of ^{155}Gd could be expected to provide a clarification of this somewhat puzzling result.

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2. Samples and experimental techniques

The preparation of samples started from a basic glass composition of 80 mol% B₂O₃ and 20 mol% Li₂O since it is not possible to form binary glasses of Gd₂O₃ and B₂O₃ alone because of an immiscibility gap [4]. B₂O₃ and Li₂CO₃ were melted and degassed for 4 d in a Pt/Rh crucible at temperatures up to 1000 K in a muffle furnace. The melt was then homogenized for 2 d at 1300 K and finally quenched in a steel form.

Powder samples of the basic glass were mixed with Gd₂O₃ (0.1, 1.0, 2.0, and 10.0 mol%, respectively). For Gd₂O₃ concentrations from 1 to 10 mol%, natural Gd which contains 14.8% ¹⁵⁵Gd was used. The sample with the lowest Gd concentration of 0.1 mol% Gd₂O₃ was prepared with oxide isotopically enriched to 92.8% ¹⁵⁵Gd. Mixtures containing 0.1–2.0 mol% Gd₂O₃ were melted in a Pt/Rh crucible at 1300 K. They were held at this temperature for 3 d. The sample with 10 mol% Gd₂O₃ was heated inductively in a graphite crucible to 1400 K for about 1 h. Finally, the hot melts were dropped on a water-cooled steel block. Estimated cooling rates achieved were about 10 K s⁻¹.

Absorbers for Mössbauer spectroscopy were prepared by filling ground glass powder into Al cans. The absorber thickness was in the range 4–15 mg cm⁻² ¹⁵⁵Gd. Mössbauer spectra for the 86.5 keV transition were recorded with a conventional constant-acceleration spectrometer in an He bath cryostat. The velocity scale was determined with a Michelson interferometer. The source, ¹⁵⁵Eu:Pd was immersed in the liquid He. Absorber temperatures T_A were 1.5 and 4.2 K for all samples. For the absorbers containing 0.1 and 2.0 mol% Gd₂O₃ spectra were also taken for $T_A = 50$ K. The spectra were analysed by least-squares fits of the transmission integral.

3. Results

All Mössbauer spectra obtained are characterized by a sizeable quadrupole splitting and by line broadening indicating a distribution of electric field gradients (figure 1).

For the 86.5 keV transition of ¹⁵⁵Gd, only the splitting S_0 of the nuclear ground state with spin $I_g = \frac{3}{2}$

$$S_0 = \frac{1}{2}eQ_g|V_{zz}|(1 + \frac{1}{3}\eta^2)^{1/2}c/E_\gamma \quad (1)$$

is resolved. Here, $Q_g = (1.30 \pm 0.02)b$ is the quadrupole moment of the nuclear ground state [5], V_{zz} is the largest component of the field-gradient tensor in diagonal form, and $\eta = (V_{xx} - V_{yy})/V_{zz}$ is the asymmetry parameter in conventional notation [6]. In principle, more detailed information on the values of η and V_{zz} , and on the sign of V_{zz} can be derived from the splitting of the excited nuclear state with spin $I_e = \frac{5}{2}$. However, the quadrupole moment of the 86.5 keV state of ¹⁵⁵Gd, $Q_e = (0.11 \pm 0.01)b$, is very small, and the splitting of the excited state is not resolved. Thus, under purely quadrupolar splitting, the Mössbauer spectra for the 86.5 keV transition of ¹⁵⁵Gd consist of two lines separated by S_0 as given in equation (1).

In a glass, variations of the local coordination from site to site are expected to give rise to a distribution of the parameters V_{zz} and η . For the case of maximally random coordination, the appropriate distribution function $P(V_{zz}, \eta)$ has been derived by Czjzek et al [7]. For the distribution of S_0 , the distribution function simplifies to

$$P(S_0) = \frac{8}{3}(S_0^4/\sqrt{\pi}\sigma^5) \exp[-(S_0/\sigma)^2]. \quad (2)$$

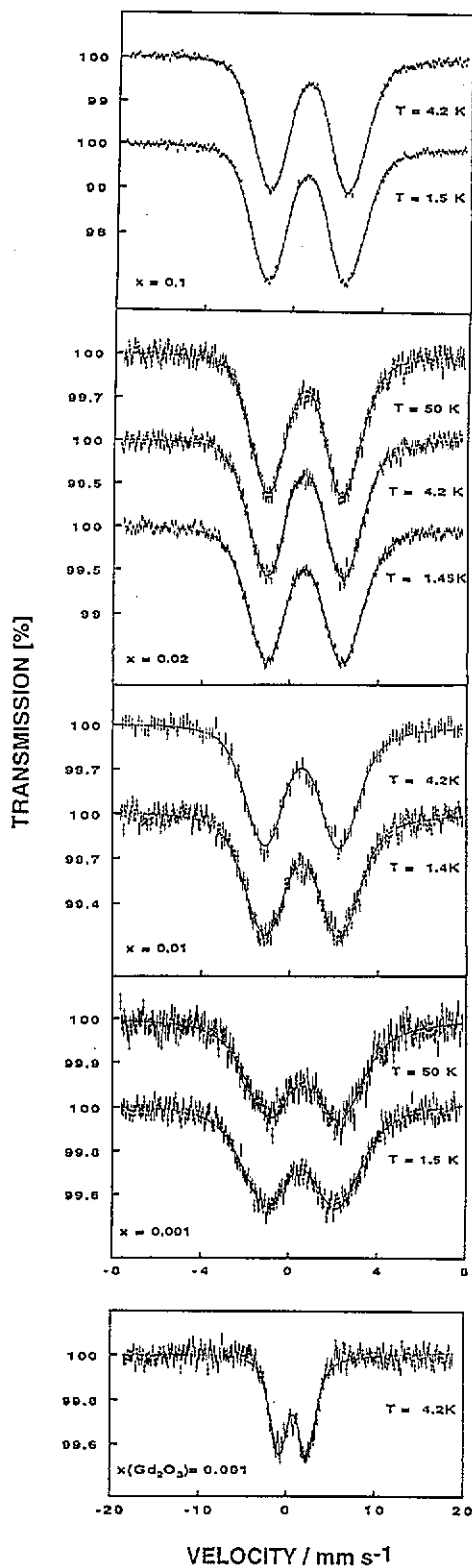


Figure 1. Mössbauer spectra of ^{155}Gd in lithium-borate glasses containing molecular concentrations x of Gd_2O_3 for absorber temperatures indicated in the figure.

This function has a maximum for $S_0 = \sqrt{2}\sigma$. The average value of S_0 is given by

$$\langle S_0 \rangle = \frac{8}{3}\sigma/\sqrt{\pi} = 1.505 \sigma \quad (3)$$

and the RMS width of the distribution is

$$(\langle S_0^2 \rangle - \langle S_0 \rangle^2)^{1/2} = (\frac{5}{2} - 64/9\pi)^{1/2}\sigma = 0.486 \sigma = 0.323\langle S_0 \rangle. \quad (4)$$

The spectra were fitted as a superposition of components corresponding to nine different values of the splitting S_0 in the range from $S_0^{(1)} = (2\sqrt{2}/9)\sigma$ to $S_0^{(9)} = 2\sqrt{2}\sigma$ (with constant increments $S_0^{(n+1)} - S_0^{(n)}$) with relative intensities as given by equation (2). The parameter σ , the isomer shift δ_{IS} , the width Γ_A of individual resonance lines, and the intensity factor f_A were adjusted in the fitting procedure, assuming the same values of δ_{IS} , Γ_A , and f_A for all components. The results obtained are summarized in table 1. The calculated spectra, shown as full curves figure 1, agree well with the experimental data.

Table 1. Results deduced from ^{155}Gd Mössbauer spectra in lithium-borate glasses containing 100x mol% Gd_2O_3 , fitted with a random distribution of quadrupole splittings with the distribution function given in equation (2). Standard deviations are given in parentheses, in units of the last displayed digit of the parameter value.

$x(\text{Gd}_2\text{O}_3)$	$T(\text{K})$	f_A	$\delta_{IS} (\text{mm s}^{-1})$	$\sigma (\text{mm s}^{-1})$	$\Gamma_A (\text{mm s}^{-1})$	$\lambda_R (\text{GHz})$
0.001	1.5	0.14(1)	0.55(2)	1.16(1)	1.57(4)	0.59(3)
	4.2	0.13(1)	0.59(2)	1.15(1)	1.37(6)	0.70(5)
	50	0.067(7)	0.60(2)	1.16(1)	1.51(6)	0.62(5)
0.01	1.4	0.14(1)	0.57(1)	1.23(1)	0.91(3)	1.2(1)
	4.2	0.13(1)	0.59(1)	1.23(1)	0.74(4)	1.6(2)
0.02	1.45	0.14(1)	0.582(2)	1.24(1)	0.64(1)	2.0(1)
	4.2	0.13(1)	0.585(6)	1.26(1)	0.48(2)	3.4(3)
	50	0.076(8)	0.565(7)	1.24(1)	0.49(2)	3.3(3)
0.10	1.5	0.14(1)	0.563(3)	1.28(1)	0.348(7)	8.0(6)
	4.2	0.14(1)	0.564(3)	1.29(1)	0.274(7)	33(10)

Attempts to calculate spectra with the model that had been found to yield qualitative agreement with experimental spectra in the study of analogous borate glasses containing EuO by ^{151}Eu Mössbauer spectroscopy [3] did not even approximately reproduce the experimental ^{155}Gd Mössbauer spectra.

4. Discussion

Values of the isomer shift, about 0.55–0.6 mm s^{-1} , are in the range typical for ionic Gd compounds, close to the shifts found in Gd_2O_3 and other oxides [8]. No significant variation with Gd content is seen.

Similarly, the recoilless fraction f_A does not vary with x . The analysis of the values given in table 1 in terms of a Debye model yields the Debye temperature $\Theta_D = (230 \pm 10)$ K. This value is somewhat smaller than that for Gd_2O_3 , $\Theta_D(\text{Gd}_2\text{O}_3) \sim 260$ K [14].

The good description of the shapes of the experimental spectra by the distribution of the splitting parameter S_0 corresponding to random coordination, equation (2), indicates

that the Gd ions are coordinated with a rather large number of irregularly arranged ligands. Unfortunately, the conclusive power of ¹⁵⁵Gd Mössbauer spectra is severely limited due to the lack of information on the distribution of the asymmetry parameter η and on the sign of V_{zz} . Yet, our conclusion is supported by results derived from EPR spectra of Gd³⁺ and Eu²⁺ ions in silicate glasses [9]. In this work, the EPR spectra were shown to be very well described by a distribution of crystal-field parameters b_2^0 (corresponding to V_{zz}) and $\lambda' = b_2^2/b_2^0$ (corresponding to η) whose features match perfectly with those of the distribution function $P(V_{zz}, \eta)$ derived for the case of random coordinations in [7].

The results for σ —and consequently for the average splitting $\langle S_0 \rangle$, according to equation (3)—increase systematically with increasing Gd content x . The cause can either be a decrease of the distance between Gd and its ligands with increasing x or, according to the results of computer simulations in [7], a decreasing coordination number with increasing x .

The distribution of quadrupole splittings is not the sole cause for broadening of resonance lines in the Mössbauer spectra. The spectrum of the sample with 10 mol% Gd₂O₃ at 4.2 K is well described by a linewidth $\Gamma_A = (0.274 \pm 0.007)$ mm s⁻¹ for the individual components of the distribution, close to the natural linewidth $\Gamma_{\text{nat}} = 0.25$ mm s⁻¹. However, the entries in table 1 clearly show that the width Γ_A of these components increases systematically with decreasing Gd content. Furthermore, for the samples with $x = 0.001$ and $x = 0.02$, the widths at 4.2 K and at 50 K are practically equal. These observations suggest slowing down of moment relaxation rates due to spin-spin interactions as the main cause of this broadening. As the lines appear to be only broadened, with no recognizable splitting, relaxation effects can be treated in the limit of fast relaxation, which applies when the relaxation rate λ_R is much larger than the frequency $\omega_{\text{HF}} = B_{\text{HF}}\mu_N|g_e m_e - g_g m_g|$ corresponding to the magnetic hyperfine splitting. With the known values of the g factors of ¹⁵⁵Gd nuclear states [10], and with $B_{\text{HF}} = 32$ T for the magnetic hyperfine field [11], we obtain for the transition between the nuclear levels $m_g = \frac{3}{2}$ and $m_e = \frac{5}{2}$ which gives the dominant contribution to the broadening; $\omega_{\text{HF}} \simeq 0.4$ GHz. In the limit of fast relaxation, the relation between λ_R , ω_{HF} , and the linewidth Γ_A is given by [12]

$$\lambda_R = 2\omega_{\text{HF}}^2/(\Gamma_A - \Gamma_0). \quad (5)$$

In this relation, Γ_0 is a reference linewidth, the natural linewidth plus any broadening due to causes other than relaxation. In our fitting procedure, broadening due to the distribution of quadrupole splittings is explicitly treated and must not be accounted for in Γ_0 . However, some broadening due to variations of isomer shifts with varying coordination numbers cannot be excluded. In the absence of information on this contribution to the linewidth, we have estimated values for the relaxation rate λ_R setting $\Gamma_0 = \Gamma_{\text{nat}}$ (last column in table 1). These estimates of λ_R must be considered as lower limits, in particular for the sample with the highest Gd content, $x = 0.1$, for which Γ_A is not much larger than Γ_{nat} .

With the exception of the glass with lowest Gd content ($x = 0.001$), significant additional broadening is found in the spectra for absorber temperatures $T_A \simeq 1.5$ K. Hence, relaxation rates at this temperature appear to be reduced compared to those at 4.2 K. The cause of this additional broadening is not quite clear. Its absence for the lowest Gd concentration is an indication that interactions between Gd moments may lead to their freezing near this temperature. In this case, however, the strongest broadening is expected for the highest Gd content, in disagreement with the experimental data. Possibly, the higher annealing temperature chosen in the preparation of the glass with 10 mol% Gd₂O₃ has led to a more homogeneous distribution of Gd ions in this sample than in the other materials

studied. Clustering of Gd ions in the samples with lower Gd content could enforce the tendency to freezing of the moments.

In these highly diluted ionic glasses, spin-spin interactions are expected to be dominated by dipolar interactions. Then, the relaxation rate is related to the distance r_{ij} between moments i and j by $\lambda_R \propto r_{ij}^{-6}$ [13]. For a homogeneous distribution of magnetic ions, this implies that λ_R is related to the concentration x of magnetic species by $\lambda_R \propto x^2$. As shown in figure 2, this relation does not hold for the relaxation rates deduced from the widths of the resonance lines in the Mössbauer spectra for the absorber temperature $T_A = 4.2$ K. Several causes may contribute to this discrepancy. Firstly, for the sample with 10 mol% Gd_2O_3 , the true relaxation rate may be significantly higher if a distribution of isomer shifts contributes to Γ_0 in equation (5). For any reasonable value of Γ_0 , which must definitely be smaller than the width Γ_A deduced from the spectrum of the sample with $x = 0.1$, the relaxation rates calculated for the other samples remain unaffected. Secondly, for the glasses containing 1 and 2 mol% Gd_2O_3 , clustering as indicated by the strong broadening of resonance lines at 1.5 K may also lead to enhanced relaxation rates. Finally, for the most diluted glass, the value deduced for the relaxation rate, $\lambda_R = 0.7$ GHz, is quite close to $\omega_{HF} = 0.4$ GHz, and the derivation assuming the limit of fast relaxation may well be inappropriate.

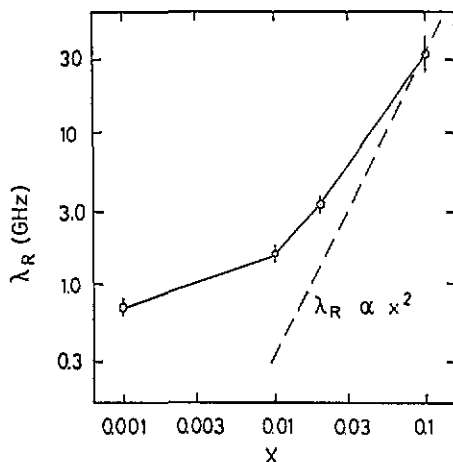


Figure 2. Relaxation rates λ_R deduced from linewidths of the spectra obtained at 4.2 K as function of the Gd concentration x . Straight lines joining data points serve as guides to the eye. The dashed line marks the concentration dependence $\lambda_R \propto x^2$ expected for spin-spin relaxation rates dominated by dipolar interactions.

5. Summary

Although the information which can be deduced from ^{155}Gd Mössbauer spectra about the distribution $P(V_{zz}, \eta)$ is rather restricted, our spectra point to a highly random distribution of ligands in the coordination shell of Gd ions in the borate glasses studied. This is in accordance with results derived from EPR spectra of Gd^{3+} ions in silicate glasses [9]. As pointed out by Brodbeck and Iton [9], this kind of coordination is expected if Gd ions are network modifiers in these glasses.

Considerable broadening beyond that resulting from the distribution of quadrupole splittings is observed. The widths of resonance lines increase rapidly as the Gd concentration is lowered. This is interpreted as a consequence of spin-spin relaxation at rates λ_R , which decrease with increasing distance between the Gd moments. Estimates of λ_R have been

obtained from the observed linewidth using the approach appropriate in the case of fast relaxation. Proportionality between λ_R and x^2 , the square of the Gd concentration, expected for dipolar interactions, is not found. Several causes may contribute to the deviation of the concentration dependence of λ_R from the expected behaviour.

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