^{155}Gd Mössbauer effect in AlB$_2$-type GdGa$_{2-x}$Al$_x$ compounds

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Abstract

We have investigated the effect of Al substitution on the lattice constants and ^{155}Gd Mössbauer spectra of GdGa$_2$. Marked changes were observed in the values of the electric field gradient derived from the quadrupole splitting of the spectra, changing from positive to negative for $x > 0.5$ in GdGa$_{2-x}$Al$_x$. This was ascribed to the concomitant change in nearest-neighbour configuration of the Gd atoms in this series, as deduced from the jump-like change in lattice parameters around $x = 0.5$. The variation in V_{zz} across the series GdGa$_{2-x}$Al$_x$ is discussed in relation to the second-order crystal field parameter A_2^0 which shows a similar variation and sign reversal.

1. Introduction

^{155}Gd Mössbauer spectroscopy is often used to obtain information on the local field gradient present at the nuclear rare earth site in various types of intermetallic compounds [1–3]. If one makes the assumption that the field gradient at the nuclear site can give information on the electric field gradient present at the site of the 4f electron charge cloud, the Mössbauer data can be helpful in the determination of the sign and magnitude of the crystal-field-induced rare earth lattice anisotropy.

The relation between the field gradient seen by the nucleus and the field gradient seen by the 4f electrons is, however, not a simple one. Band structure calculations made on several compounds [1] have revealed that there is no physical basis for assuming the applicability of a relation of the type $A_2^0 = -V_{zz}(1 - \sigma_2)/4(1 - \gamma_\infty)$ as was done frequently in the past. The absence of such a proportionality relation strongly hampers the use of the relatively simple rare earth Mössbauer spectroscopy for studying the macroscopic magnetic anisotropy in rare-earth-based systems. Although the band structure calculations revealed that principally no proportionality relation between A_2^0 and V_{zz} exists, they simultaneously showed that numerically about the same ratio A_2^0/V_{zz} is found in 3d-rich rare earth compounds closely related in structure and composition [2]. It is the purpose of the present investigation to study the behaviour of V_{zz} in a completely different system in which rare earths are combined exclusively with s, p elements. The system RGa$_{2-x}$Al$_x$ appears to be most suitable for this purpose, since reliable experimental values of the crystal field parameter A_2^0 are available [4] which can be compared directly with experimental values of V_{zz} derived from ^{155}Gd Mössbauer spectroscopy.

2. Experimental details

The GdGa$_{2-x}$Al$_x$ compounds studied in this investigation were prepared by arc melting from starting materials of at least 99.9% purity. All compounds were vacuum annealed at 800 °C for several weeks. After vacuum annealing, the samples were examined by X-ray diffraction to check whether single-phase compounds had formed. The AlB$_2$-type structure was observed for all GdGa$_{2-x}$Al$_x$ compounds with $x \leqslant 1.5$. The X-ray diagram of the compound GdGa$_{0.5}$Al$_{1.5}$ contained diffraction lines of the cubic MgCu$_2$-type structure (main phase) together with lines of the AlB$_2$ structure. For this reason the latter compound was not included in the Mössbauer study.

Mössbauer spectra of the various AlB$_2$-type compounds were taken by using the 86.5 keV resonance of ^{155}Gd. Our source consisted of neutron-irradiated SmPd$_3$ prepared from samarium enriched to 98% in ^{154}Sm. Details of the spectrometer have been described elsewhere [5].

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All spectra have been analysed by means of a least-squares-fitting procedure comprising diagonalization of the full nuclear hamiltonian and use of a transmission integral. The independently refined variables consisted of the isomer shift (IS), the effective hyperfine field (H_{eff}) and the quadrupole splitting (QS). From the last quantity the electric field gradient tensor element V_{zz} was obtained via the relation $QS = \frac{1}{4}eQV_{zz}(3 \cos^2\theta - 1)$ using the value $Q = 1.30 \times 10^{-28}$ m^2 given by Tanaka et al. [6]. The angle θ between H_{eff} and the c axis was kept as an adjustable parameter. The linewidths of the absorber and source were constrained to 0.25 and 0.36 mm s^{-1} respectively for the transmission integral.

3. Experimental results

The lattice constants derived from the single-phase AlB$_2$-type compounds have been plotted as a function of the concentration in Fig. 1. It is seen that these lattice constants show a dramatic discontinuity around $x = 0.6$. The X-ray diagrams of the compounds with $x = 0.60$ and 0.75 consisted of a mixture of reflections
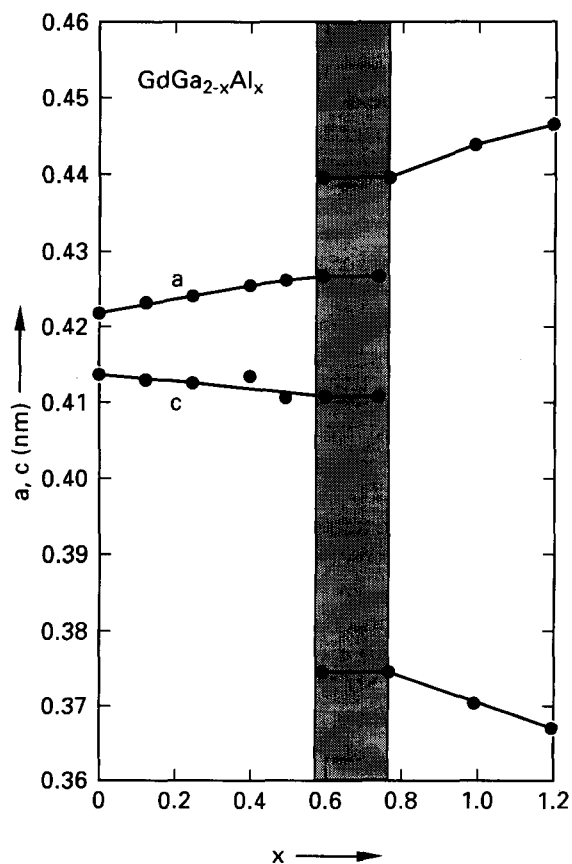

Fig. 1. Concentration dependence of the lattice constants in the series of compounds GdGa$_{2-x}$Al$_x$. The shaded concentration region indicates the coexistence of the crystallographic forms with high and low c/a ratio.

belonging to the two crystallographic forms with high and low c/a ratio respectively. The presence of a two-phase region shows that the two forms can coexist with each other. The compound with $x = 0.60$ contained less than 10% of the form with low c/a ratio. The compound with $x = 0.75$ contained less than 3% of the form with high c/a ratio. The approximate extent of the two-phase region has been indicated in Fig. 1.

The ^{155}Gd Mössbauer spectra obtained at 4.2 K from the AlB$_2$-type compounds are shown in Fig. 2. It may be seen from the figure that the general shape of the spectra for the compounds with $x < 0.6$ is different from those of higher Al concentration. The hyperfine parameters derived from fitting the spectra are listed in Table 1. Inspection of the values of the hyperfine parameters shows that there is a sign reversal of V_{zz}. This is seen more clearly in Fig. 3, where the values of V_{zz} are plotted vs. Al concentration. From the fitting of the spectrum of the compound with $x = 0.5$ the sign of V_{zz} for this compound could not be determined unambiguously. Clearly the sign reversal has to be associated with the marked jump in the lattice constants shown in Fig. 1. For this reason we have assumed that V_{zz} for the compound with $x = 0.5$ is still positive in the plot of Fig. 3.

^{155}Gd Mössbauer spectra of all compounds were measured also in the paramagnetic regime (at 77 K). Results are shown in Fig. 4. Since the effective hyperfine fields have vanished in these cases, one finds that the spectra show only quadrupolar splitting. The corresponding values of V_{zz} are included in Table 1. In most cases there is a decrease in V_{zz} of roughly 20% on going from 4.2 K to 77 K, except for GdGa$_2$ where the decrease is considerably more pronounced. This feature will be examined more closely in a forthcoming investigation.

4. Discussion

The sign reversal of the electric field gradient observed at the nuclear Gd site in GdGa$_{2-x}$Al$_x$ is quite unusual and undoubtedly originates from the strong variation in the lattice constants as shown in Fig. 1. Although we cannot offer an explanation for this strong variation in the lattice constants, we wish to mention here that it is not restricted to the series GdGa$_{2-x}$Al$_x$ but has been observed in several other series of pseudobinary compounds RGa$_{2-x}$Al$_x$ with R $\equiv$ Ce [7], Nd [8, 9], Dy [4], Ho [4] and Er [9]. The strong jump in the lattice constants displayed in Fig. 1 has as a consequence that there is a marked change in the nearest-neighbour configuration of the Gd atoms. This change in nearest-neighbour configuration may be illustrated by means of Fig. 5, where the nearest-neighbour configuration is shown for the cases $c/a < 1$, $c/a = 1$ and $c/a > 1$.
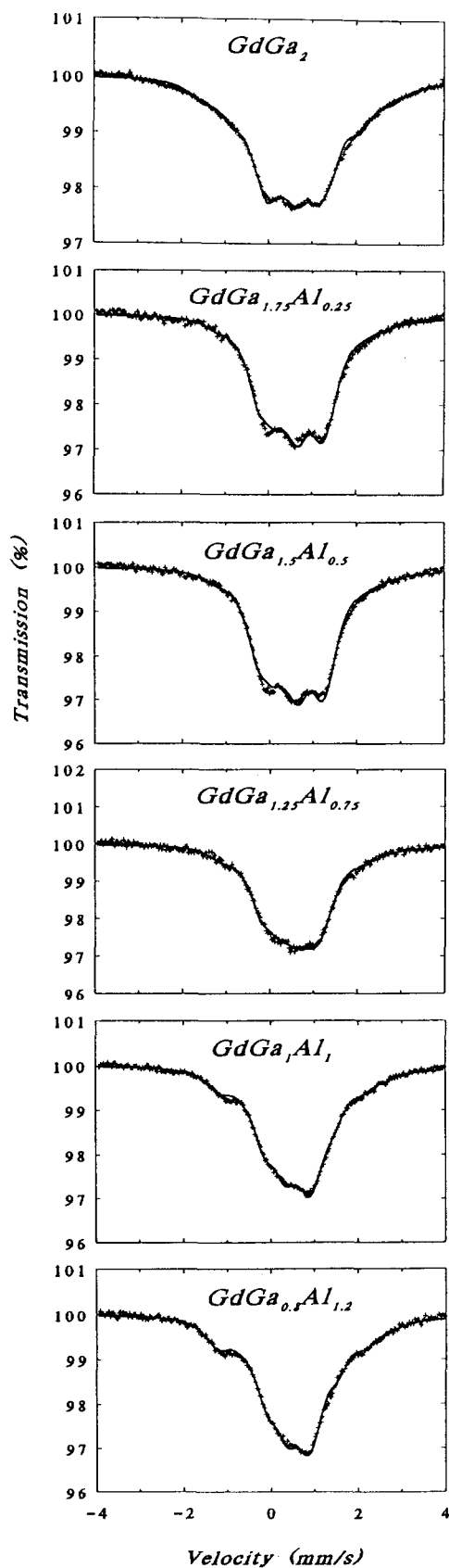
Fig. 2. Development of the ^{155}Gd Mössbauer spectra (4.2 K) with Al concentration in GdGa$_{2-x}$Al$_x$.

TABLE 1. Hyperfine parameters derived from fits of the ^{155}Gd Mössbauer spectra of several representative GdGa$_{2-x}$Al$_x$ compounds with the AlB$_2$ structure at 4.2 and 77 K

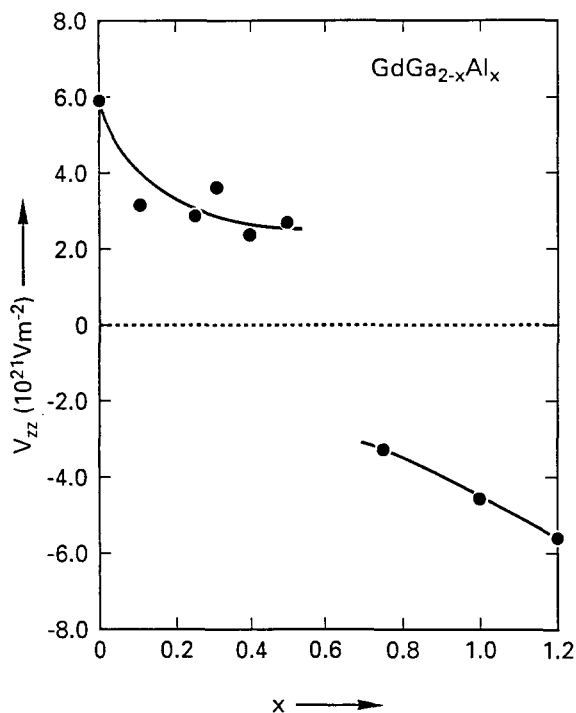| x	T (K)	V_{zz} (10^{21} V m^{-2})	$\mu_0 H_{eff}$ (T)	θ (deg)	IS (mm s^{-1})
0.00	4.2	+ 5.9	33.3	51	0.59
	77	+ 3.2	0	—	0.60
0.25	4.2	+ 2.9	28.0	48	0.58
	78	+ 2.6	0	—	0.59
0.50	4.2	+ 2.7	28.3	90	0.57
	77	+ 2.1	0	—	0.57
0.75	4.2	− 3.3	34.9	90	0.53
	77	− 2.7	0	—	0.54
1.00	4.2	− 4.6	26.1	90	0.52
	77	− 4.0	0.0	—	0.51
1.20	4.2	− 5.5	25.7	90	0.51
	77	− 4.7	0.0	—	0.50

Fig. 3. Concentration dependence of the electric field gradient V_{zz} in GdGa$_{2-x}$Al$_x$ at 4.2 K.

In several previous reports it was shown that the electric field gradient at the nuclear site of the Gd atoms in Gd metal and in several types of intermetallic compounds is mainly determined by the aspherical charge distribution of the on-site 5d and 6p valence electrons [1, 2, 10]. It is reasonable to assume that the field gradient in the compounds studied in the course of the present investigation has a similar origin.
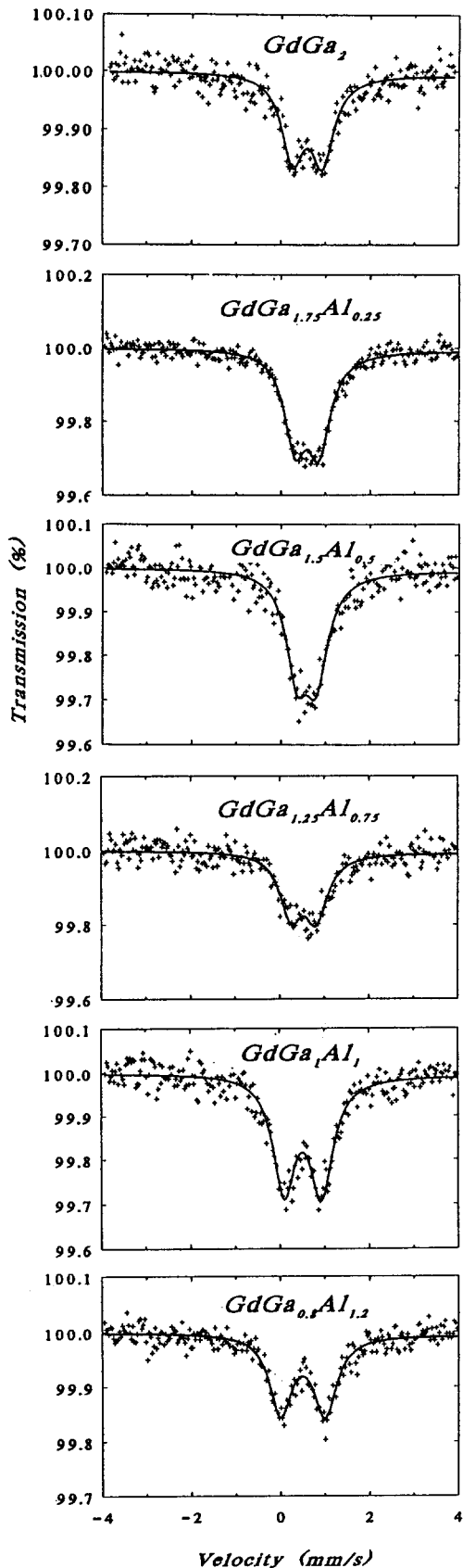
Fig. 4. Development of the quadrupole splitting with Al concentration in the ^{155}Gd Mössbauer spectra of GdGa$_{2-x}$Al$_x$ at 77 K.

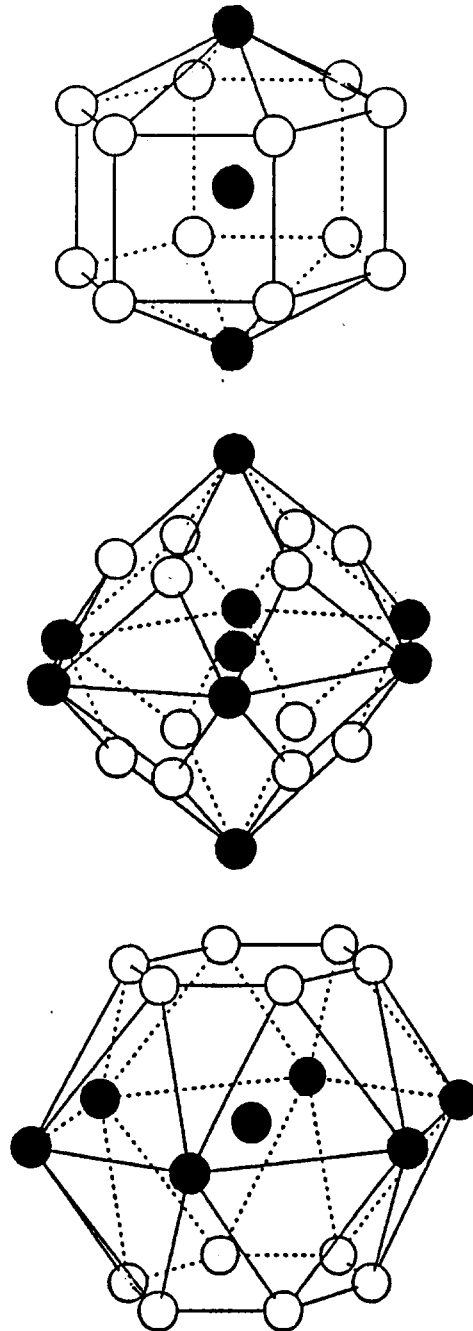Fig. 5. Change in coordination of the central Gd atom with c/a ratio in the AlB$_2$ structure type: ●, Gd; ○, Ga, Al.

Inspection of the schematic representation of the nearest-neighbour configuration shown in Fig. 5 suggests that there will be no major changes in the 5d and 6p asphericities due to Ga (Al) on going from the situation $c/a \approx 1$ to the situation $c/a \leqslant 1$. The most prominent changes affect the nearest-neighbour Gd atoms, bearing in mind that to reach the situation $c/a < 1$, not only is contraction of the c axis necessary but also expansion of the a axis. The overlap of the 5d and 6p wavefunctions of the central Gd atom with those of the Gd neighbour

atoms will therefore be strongly reduced in the a direction and strongly increased in the c direction. In the spirit of results obtained earlier [1], these changes entail a shift of V_{zz} towards more negative values, as is observed experimentally (see Fig. 3).

A point of considerable importance is the relation between V_{zz} and the second-order crystal field parameter $A_2{}^0$. Both quantities are a measure of the electric field gradient, the former at the nuclear site, the latter at the site of the 4f electrons. However, the relative charge densities of the 5d and 6p electrons are different at the two sites. Consequently it is physically not realistic to write

$$A_2{}^0 = -\omega V_{zz} \tag{1}$$

where ω is a proportionality constant. A relation of this type is expected to hold approximately only if the relative charge densities of the 5d and 6p electrons at the nuclear site and the 4f site do not change much from one compound to another and the 5d and 6p charge asphericities are roughly the same. Such a situation cannot be excluded a priori. In fact, a comparison of experimental values of $A_2{}^0$ (K $a_0{}^{-2}$) and V_{zz} (10^{21} V m^{-2}) for several 3d-rich rare earth compounds of closely related crystal structure and similar composition has shown that relation (1) is reasonably well obeyed with $\omega = 46$ [2].

It would be of much interest to check to what extent relation (1) holds also for compounds in which rare earth elements are combined exclusively with s, p metals, e.g. R(Ga, Al)$_2$. Reliable experimental values of $A_2{}^0$ for several of these compounds (R $\cong$ Dy, Ho) were obtained recently on the basis of various complementary experimental techniques, including magnetic measurements on single crystals, inelastic neutron scattering and specific heat measurements [4]. Results obtained in ref. 4 for DyGa$_2$ and DyGaAl have been listed in Table 2. On using these values and the V_{zz} values listed

for the corresponding Gd compounds in Table 1, one finds that ω of relation (1) is roughly the same for both sets of compounds. This is a very satisfactory result, since it shows that not only the sign reversal of V_{zz} and $A_2{}^0$ but also the absolute values of both quantities vary in a consistent manner on going from RGa$_2$ to RGaAl.

The value $\omega = 35$ is of the same sign but somewhat smaller in magnitude than the value $\omega = 46$ obtained previously for several compounds of the type R$_2$Co$_{17}$Z$_x$ and R$_2$Fe$_{17}$Z$_x$, where Z represents interstitial carbon or nitrogen atoms [2]. Here one has to bear in mind that the rare earth compounds RGa$_2$ and R$_2$Co$_{17}$ (or R$_2$Fe$_{17}$) are totally different with respect to the partner element and with respect to the crystal structure. However, even under such extremely different conditions the proportionality constant ω has retained the same sign and approximately the same magnitude. This lends credence to procedures in which experimental values of V_{zz} derived from the quadrupolar splitting of rare earth Mössbauer spectra are used to predict the sign and magnitude of the experimentally less accessible crystal field parameter $A_2{}^0$, despite the fact that the basis of the relationship between V_{zz} and $A_2{}^0$ has to be reconsidered.

TABLE 2. Experimental values of $\langle r^2 \rangle A_2{}^0$ for DyGa$_2$ and DyGaAl as reported in ref. 4. The values of ω are discussed in the text

	DyGa$_2$	DyGaAl
$\langle r^2 \rangle A_2{}^0$ (K)	−144.9	116.5
$A_2{}^0$ (K $a_0{}^{-2}$)	−199.5	160.5
ω	34	35

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