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^{155}Gd Mössbauer effect and magnetic properties of aluminium- and gallium-substituted $GdCu_5$ and $GdNi_5$

F. M. Mulder and R. C. Thiel
Kamerlingh Onnes Laboratory, Leiden University, NL-2300 RA Leiden (Netherlands)

K. H. J. Buschow
Philips Research Laboratories, NL-5600 JA Eindhoven (Netherlands)

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Abstract

We have investigated the effect of aluminium and gallium substitution on the ^{155}Gd Mössbauer spectra of $GdCu_5$ and $GdNi_5$. No marked changes were observed in the values of the electric field gradient derived from the quadrupole splitting of the spectra. This was ascribed to the absence of a strongly preferred substitution of aluminium and gallium into one of the two available non-rare earth sites in $GdNi_5$ and $GdCu_5$. Additional evidence for this was obtained from X-ray diffraction. Further analysis of our data has shown that the earlier reported phase transition in $GdCu_5$ at low temperatures is probably non-existent.

1. Introduction

In several investigations we have used ^{155}Gd Mössbauer spectroscopy to obtain information on the local field gradient present at the nuclear rare earth site in various types of intermetallic compounds [1–3]. These studies have been motivated by the possibility that ^{155}Gd Mössbauer spectroscopy can also provide information on the electric field gradient present at the side of the 4f electron charge cloud and hence provide information on the sign and magnitude of the crystal-field-induced rare earth lattice anisotropy. The latter quantity is of considerable importance in rare-earth-based permanent magnet materials and has led to the formulation of the important questions of how to identify structures and the corresponding rare earth atom coordinations, in which the electric field gradient has a large magnitude.

Of much relevance in this respect is a still-unsolved problem reported several years ago for the compound $GdCu_5$. This compound was reported to have the hexagonal $CaCu_5$-type structure and its ^{155}Gd Mössbauer spectra gave evidence of a phase transition of unknown origin at about 25 K [4]. This phase transition caused the electric quadrupole splitting, or equivalently the electric field gradient V_{zz}, to increase strongly from $V_{zz} \approx 0$ for $T \geqslant 25$ K to a comparatively large value for $T < 26$ K ($V_{zz} = -5.9 \times 10^{21}$ V cm^{-2} at 4.2 K). Results of this investigation are reproduced in Fig. 1, from which it may be inferred that the effective hyperfine field shows a behaviour opposite to that of V_{zz}. Here the low temperature phase has a comparatively small value of B_{hf}, whereas B_{hf} has a large value in the spectrum of the high temperature phase (Fig. 1(b)).

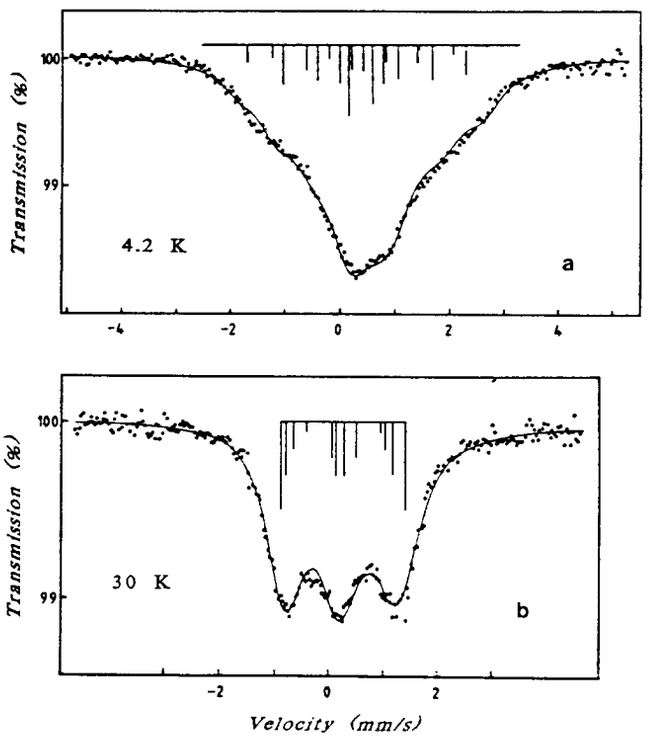

Fig. 1. Mössbauer spectra obtained on $GdCu_5$ at 4.2 K (a) and 30 K (b). Data have been reproduced from ref. 4.

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In the present investigation we have performed ^{155}Gd Mössbauer spectroscopy and magnetic measurements on several compounds of the series $GdCu_{5-x}Al_x$ and $GdCu_{5-x}Ga_x$, in order to obtain more information on the nature of the phase transition. It will be shown that the existence of a phase transition in $GdCu_5$ is a misconception and that a satisfactory interpretation of the spectra observed previously for $GdCu_5$ can be obtained by assuming the presence of two phases based on the hexagonal $CaCu_5$ type and the cubic $AuBe_5$ type. Included in this investigation are also results obtained for aluminium- and gallium-substituted $GdNi_5$.

2. Experimental details

The compounds studied in these investigations were prepared by arc melting from starting materials of at least 99.9% purity. The compound $GdNi_3Ga_2$ was vacuum annealed at 800 °C for several weeks. The compound $GdCu_5$ was too ductile to prepare a powder sample needed for Mössbauer spectroscopy. In order to obtain a sufficiently thin sample of $GdCu_5$ for the latter measurements, we used melt spinning to produce thin ribbons. In contrast, after substituting only 1 at.% of aluminium for copper ($GdCu_{4.95}Al_{0.05}$), the compound was sufficiently brittle for powdering, so that melt spinning was not necessary.

All samples used in this investigation were examined by X-ray diffraction to check if single-phase compounds had formed. The $CaCu_5$-type structure was observed for all $GdCu_{5-x}Al_x$ compounds and for $GdNi_2Al_3$ and $GdCu_3Ga_2$. The $HoNi_{2.6}Ga_{2.4}$ type was found for $GdNi_3Ga_2$.

Magnetic measurements were made only for compounds of the type $GdCu_{5-x}Al_x$. These measurements were made in the temperature range 4.2–300 K.

The Mössbauer spectra of the various compounds studied were taken by using the 86.5 keV resonance of ^{155}Gd. The source was neutron-irradiated $SmPd_3$, using samarium enriched to 98% in ^{154}Sm. Details of the spectrometer are given elsewhere [1]. All spectra have been analysed by means of a least-squares-fitting procedure involving the diagonalization of the full nuclear hamiltonian and using a transmission integral. The independently refined variables consisted of the isomer shift (IS), the effective hyperfine field (H_{eff}) and the quadrupole splitting (QS) (or the electric field gradient tensor element V_{zz}, 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.* [5]). 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 and discussion

3.1. $GdCu_{5-x}Al_x$ compounds

Owing to the fact that the X-ray patterns of cubic $AuBe_5$ type and hexagonal $CaCu_5$ type for the compounds RCu_5 are very similar, the compounds in which R is a heavy rare earth metal have been described as being hexagonal as well as being cubic [6, 7]. Structure determinations showed that the cubic structure is correct for R elements heavier than gadolinium, the remainder of the compounds crystallizing in the hexagonal structure [7]. A further complication arises for the compound $GdCu_5$, since this compound is fairly ductile and hence it is difficult to prepare powder samples for X-ray diffraction. X-ray data taken from powdered $GdCu_5$ showed considerable line broadening, which in conjunction with the similarity in X-ray pattern between hexagonal and cubic structures made it difficult to establish whether the hexagonal type is the only phase present or whether there is also a substantial fraction of the cubic phase present. This is not unlikely, since the cubic and hexagonal structures are observed for R≡Tb and Sm respectively [7], opening up the possibility that both structures may be found in $GdCu_5$. The expected low difference in stability between the two modifications of $GdCu_5$ has a further consequence,

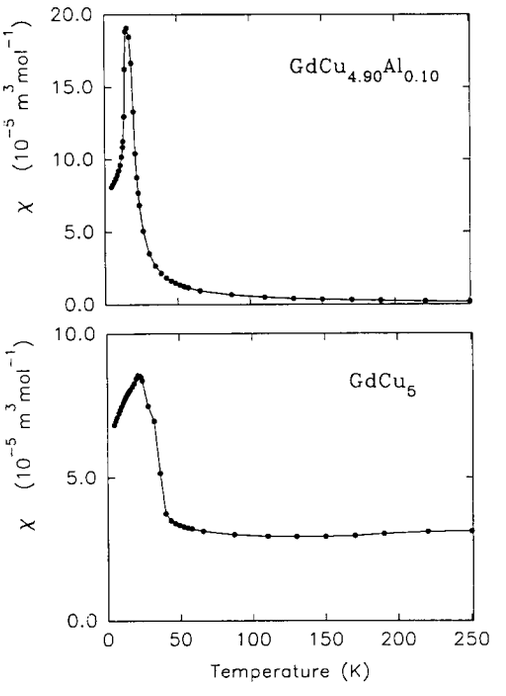

Fig. 2. Temperature dependence of the magnetic susceptibility in $GdCu_5$ (bottom) and $GdCu_{4.90}Al_{0.10}$ (top).

namely that if both the hexagonal and cubic forms are present after solidification from the melt, it will be difficult to obtain a single-phase sample of $GdCu_5$ by further annealing.

From our X-ray data on $GdCu_{5-x}Al_x$ we derive that substitution of aluminium for copper strongly stabilizes the hexagonal structure, even when aluminium is present in very small amounts. For aluminium concentrations as low as 1 at.% ($x=0.05$) the sample has become brittle and displays sharp X-ray diffraction peaks. A similar effect of aluminium is found in the magnetic properties. This may be illustrated by means of Fig. 2, where the magnetic measurements of $GdCu_5$ are compared with those of $GdCu_{4.90}Al_{0.10}$. The former material shows a strongly broadened cusp, indicating a broadened Néel-type transition. Above T_N the magnetic susceptibility remains almost temperature independent and a Curie–Weiss behaviour is not followed even approximately. In contrast, $GdCu_{4.90}Al_{0.10}$ shows a very sharp Néel-type transition, with $\chi(T)$ following a Curie–Weiss behaviour almost immediately above T_N.

Results of ^{155}Gd Mössbauer spectroscopy for $GdCu_{5-x}Al_x$ samples with $x=0.05$ and 0.1 are shown in Figs. 3 and 4 respectively. In both cases one recognizes at the lowest temperature a quadrupolar- and Zeeman-split spectrum. An increase in the temperature leads

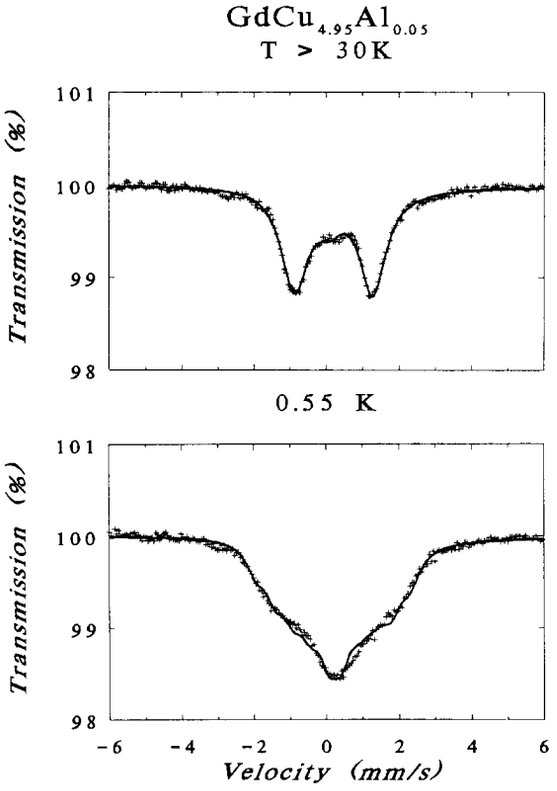

Fig. 3. ^{155}Gd Mössbauer spectra of $GdCu_{4.95}Al_{0.05}$ at 0.55 K (bottom) and above 30 K (top). The solid curve through the data points represents a fit.

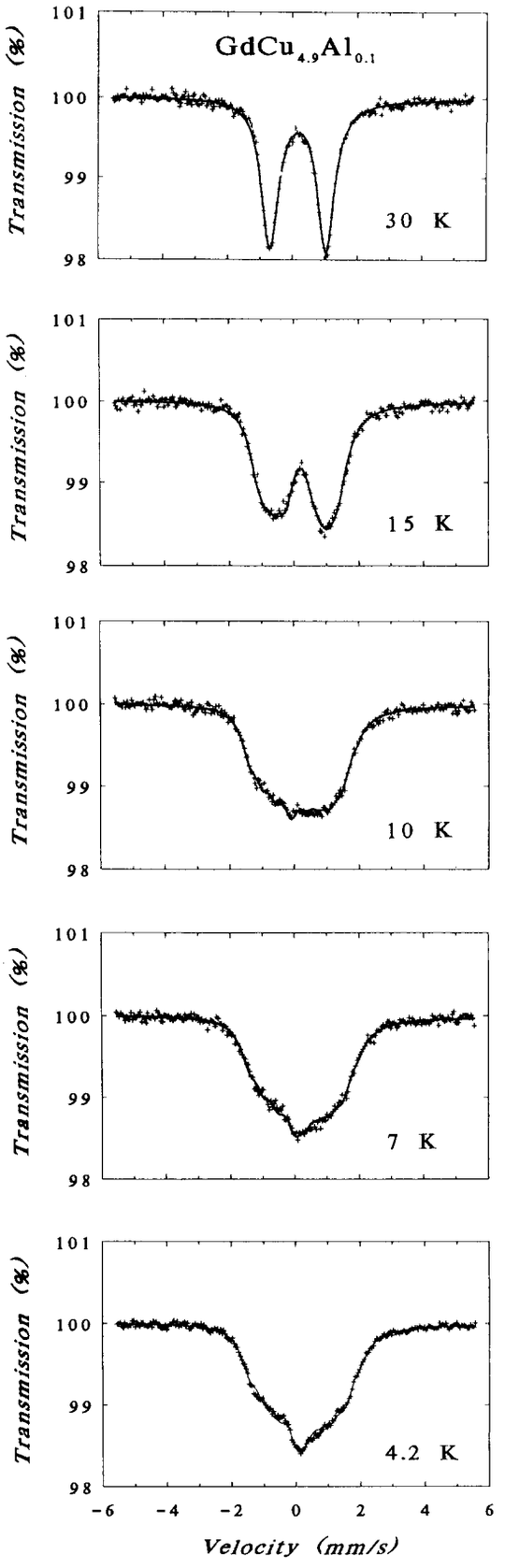

Fig. 4. Thermal variation in the ^{155}Gd Mössbauer spectra of $GdCu_{4.90}Al_{0.10}$.

TABLE 1. Hyperfine parameters derived from fits of the ^{155}Gd Mössbauer spectra of various compounds with the $CaCu_5$ structure (h*P*6), the $AuBe_5$ structure (c*F*24) or the $HoNi_{2.6}Ga_{2.4}$ structure (h*P*18). The relative intensities of the subspectra are indicated by R_I

Compound	Structure	V_{zz} (10^{21} V m^{-2})	B_{eff} (T)	IS (mm s^{-1})	θ (deg)	R_I
$GdCu_5$	h*P*6	9.8	23.2	0.25	47	0.70
	c*F*24	0.0	18.5	0.23	—	0.30
$GdCu_{4.9}Al_{0.1}$	h*P*6	8.1	20.0	0.205	44	1
$GdCu_4Al$	h*P*6	6.9	26.4	0.40	43	1
$GdCu_3Al_2$	h*P*6	5.4	27.5	0.46	37	1
$GdCu_3Ga_2$	h*P*6	7.1	26.8	0.48	43	1
$GdNi_5$	h*P*6	9.7	22.9	0.25	0	1
$GdNi_2Al_3$	h*P*6	8.4	38.9	0.50	90	1
$GdNi_3Ga_2$	h*P*18	6.9	27.8	0.35	59	0.7
		9.8	28.4	0.27	0	0.3

to the disappearance of the Zeeman splitting, leaving a quadrupole doublet in both cases. There is no indication of any structure or phase transition. As may be seen from Fig. 5, there is a smooth and continuous increase in the effective hyperfine field with decreasing temperature, indicating the onset of magnetic ordering at about 20 K, in agreement with the results of the magnetic measurements shown in Fig. 2 (top part). Results for aluminium-richer concentrations are displayed in Fig. 6. The hyperfine parameters derived from fitting the low temperature spectra have been listed in Table 1.

^{155}Gd Mössbauer spectra of the compounds $Gd_{0.1}R_{0.9}Cu_5$ were studied for R≡Ho, Er, Lu. All these compounds were shown by X-ray diffraction to be cubic. The corresponding ^{155}Gd Mössbauer spectra are shown in Fig. 7. Since none of the cubic compounds RCu_5 (R≡Lu, Er, Ho) was reported [8] to give rise to magnetic ordering above 4.2 K, one expects the Zeeman splitting to be absent or to be only comparatively small. In other words, the spectra shown in Fig. 6 can be taken as

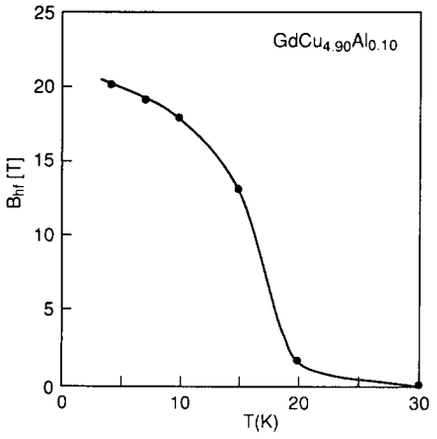

Fig. 5. Temperature dependence of the effective ^{155}Gd hyperfine field in $GdCu_{4.90}Al_{0.10}$.

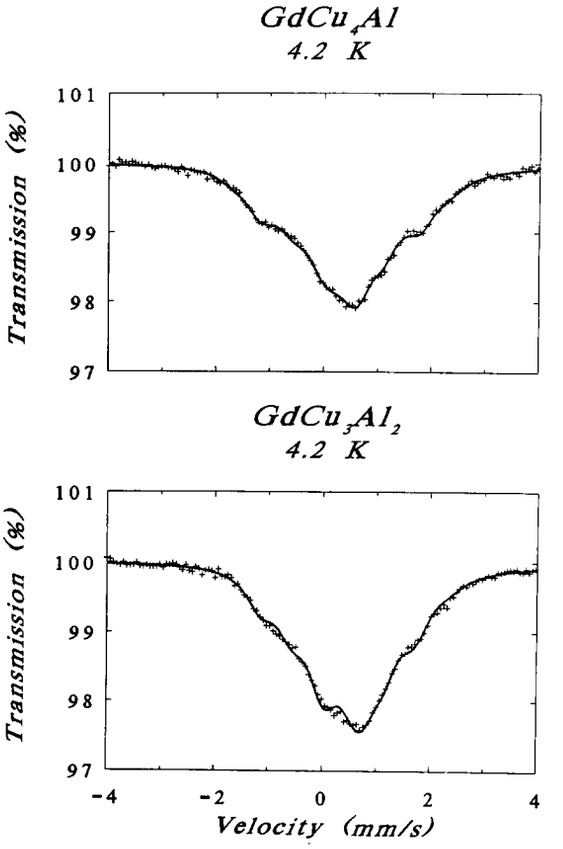

Fig. 6. ^{155}Gd Mössbauer spectra at 4.2 K of $GdCu_4Al$ (top) and $GdCu_3Al_2$ (bottom).

reflecting the general appearance of the spectrum of cubic $GdCu_5$ in the paramagnetic state. As seen from Fig. 7, this type of spectrum is characterized by a single-peaked structure, the peak position being close to zero velocity and shifted slightly towards positive velocities.

When comparing the spectra of the type shown in Fig. 7 with the spectra shown in Figs. 3 and 4, one

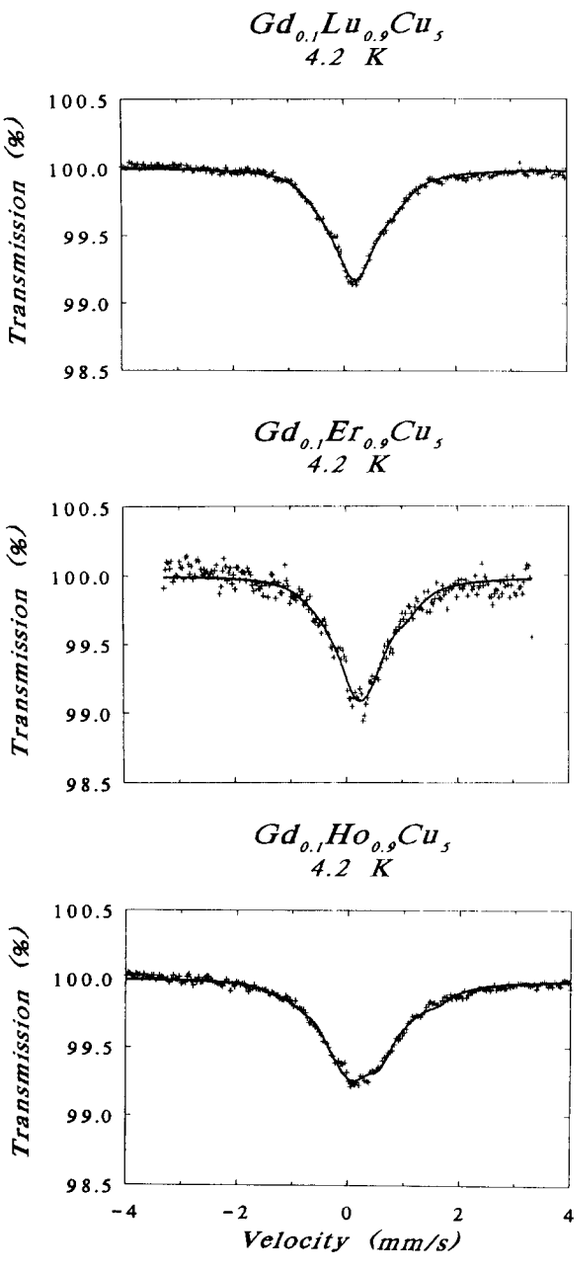

Fig. 7. ^{155}Gd Mössbauer spectra of the cubic pseudobinary compounds $Gd_{0.1}R_{0.9}Cu_5$ (R≡Lu, Er, Ho) at 4.2 K.

finds that the spectra of Fig. 1 can conveniently be interpreted as a superposition of two subspectra resulting from the simultaneous presence of cubic and hexagonal $GdCu_5$. This is most clearly seen in the 30 K spectrum of $GdCu_5$, where the double-peaked structure of the paramagnetic hexagonal phase is superimposed on the single-peaked structure of the paramagnetic cubic phase. It follows from our analysis that there is no need to assume any low temperature phase transition in $GdCu_5$.

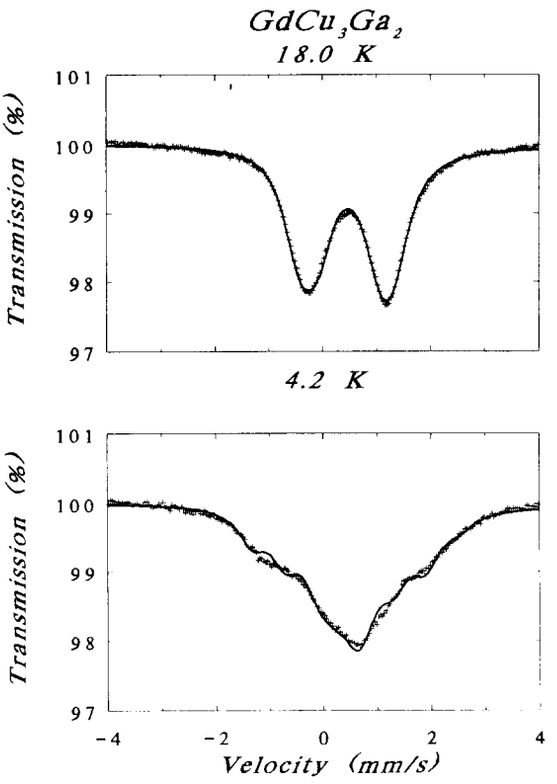

Fig. 8. ^{155}Gd Mössbauer spectra of $GdCu_3Ga_2$ at 4.2 K (bottom) and 18 K (top).

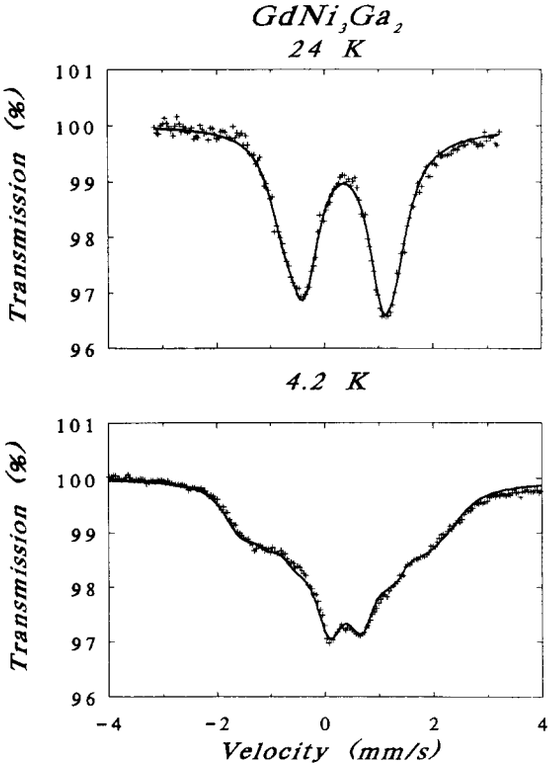

Fig. 9. ^{155}Gd Mössbauer spectra of $GdNi_3Ga_2$ at 4.2 K (bottom) and 24 K (top).

3.2. Related compounds

In the spirit of a previous investigation dealing with the electric field gradient in compounds with structures related to the $CaCu_5$ type, we have extended our investigation to the compounds $GdCu_3Ga_2$, $GdNi_2Al_3$ and $GdNi_3Ga_2$ [9].

According to our X-ray results, one may classify the first two of these compounds as belonging to the $CaCu_5$ type, with a more or less random occupation of copper (nickel) and aluminium over the two available crystallographic sites. The situation here is different from that of compounds such as $GdCo_3B_2$, where cobalt and boron are restricted to one of the two crystallographic sites. Results of $GdCu_3Ga_2$ are shown in Fig. 8 and the corresponding hyperfine parameters together with those of $GdNi_2Al_3$ are listed in Table 1. It is seen that the field gradients reached in both compounds are not much different from those of the other $CaCu_5$-type compounds.

The X-ray diagram of $GdNi_3Ga_2$ is quite distinct from those of the other compounds studied in this investigation. It shows that this compound crystallizes in the $HoNi_{2.6}Ga_{2.4}$-type structure (h*P*18), which is related to the $CaCu_5$ type but is characterized by two different rare earth sites occurring in the ratio 2:1 [10]. The ^{155}Gd Mössbauer spectra obtained at 4.2 and 24 K for this compound are displayed in Fig. 9 and the corresponding hyperfine parameters are listed in Table 1. It can be seen from the data listed that there is a distinct, though small, difference in electric field gradient at the two gadolinium sites. On the basis of the crystal structure and previous results [1], one would have expected a much larger difference in electric field gradient, since the minority gadolinium site has six nearest 3d atom neighbours in the equatorial plane ($z=0$) whereas the majority gadolinium site has six nearest Ga atom neighbours in the equatorial plane ($z=\frac{1}{2}$). However, these considerations only hold in the ideal structure of a compound of nominal composition $GdNi_2Ga_3$, where the Ni and Ga atoms are restricted to the corresponding non-equivalent crystallographic sites [10].

4. Concluding remarks

We have reinvestigated the compound $GdCu_5$, for which previous ^{155}Gd Mössbauer spectroscopy had indicated a phase transition below 25 K characterized by strong and opposite changes in the electric field gradient and the hyperfine field. The results obtained in the course of the present investigation cannot refute the existence of such a phase transition, but we have presented accumulative evidence that an interpretation of the spectral changes in terms of two coexisting phases of different crystal structures and different hyperfine parameters is more likely.

We have investigated the effect of substituting aluminium and gallium for nickel and copper in $GdNi_5$ and $GdCu_5$, respectively. These two s, p elements have a lower electron density at the Wigner–Seitz cell boundary than copper and nickel. On the basis of a simple model proposed earlier [1], one would expect the electric field gradient to be lowered or increased if the s, p elements showed a strong preference for occupying the 2*c* site (in the basal plane of the $CaCu_5$ structure) or the 3*g* site (in a plane at $z=\frac{1}{2}$ in the $CaCu_5$ unit cell) respectively. However, no pronounced changes in V_{zz} were observed, which can be explained by the reluctance of aluminium and gallium to show a strong site preference.

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