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^{155}Gd Mössbauer investigation of the compound $GdPd_2Al_3$

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Abstract

We have studied the compound $GdPd_2Al_3$ (hexagonal, $PrNi_2Al_3$ type, $a = 0.5373$ nm, $c = 0.4189$ nm) by means of ^{155}Gd Mössbauer spectroscopy. From the quadrupole splitting of the spectra we determined sign and magnitude of the electric field gradient at the nuclear site, $V_{zz} = +12.6 \times 10^{21}$ V m^{-2}. This value corresponds to a second-order crystal field parameter in the RPd_2Al_3 series equal to $A_2^0 = -440 K a_0^{-2}$.

Keywords: Mössbauer investigations; Quadrupole splitting; Crystal field parameters

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1. Introduction

In several previous papers we have used ^{155}Gd Mössbauer spectroscopy to study the behaviour of the electric field gradient (V_{ZZ}) at the nuclear site in a variety of different Gd compounds and used these results to obtain information on the crystal field splitting [1–3]. Recently compounds of the type RPd_2Al_3 have attracted much attention because of their interesting magnetic and electrical transport properties. This is true, in particular, for the compound $CePd_2Al_3$. There is contradictory information in the literature, however, regarding the crystal field splitting in these compounds [4–6]. In the present investigation we will use ^{155}Gd Mössbauer spectroscopy to obtain additional information on the crystal field interaction.

2. Experimental

The compound $GdPd_2Al_3$ was prepared by means of arc melting from starting materials of at least 99% purity. After arc melting the sample was wrapped into Ta foil and vacuum-annealed inside an evacuated quartz tube at 800 °C for four weeks. After annealing, the sample was investigated by X-ray diffraction. The X-ray pattern was indexed according to the hexagonal $PrNi_2Al_3$ type structure with the lattice constants $a = 0.5373$ nm, $c = 0.4189$ nm. A few diffraction lines, of which the total intensity was less than 5%, did not belong to the mentioned structure type and pointed to the presence of small amounts of an impurity phase.

Mössbauer spectra of the compound $GdPd_2Al_3$ were obtained at 4.2 K and 30 K by means of the 86.5 keV resonance of ^{155}Gd. The source consisted of neutron-irradiated $SmPd_3$ that had been prepared from samarium enriched to 98% in ^{154}Sm. More details of the spectrometer can be found elsewhere [7]. The two spectra have been analysed by means of a least squares fitting procedure which included the diagonalization of the full nuclear Hamiltonian and the employment of a transmission integral. The independently refined hyperfine parameters consisted of the isomer shift IS, the effective hyperfine field H_{eff} and the quadrupole splitting $QS = eQV_{zz}(3\cos^2\theta - 1)/4$. For the value of the ground state quadrupole moment we used the value $Q = 1.30 \times 10^{-28}$ reported by Tanaka et al. [8]. The angle θ between H_{eff} and the c-axis was kept as an adjustable parameter. The linewidths of absorber and source were constrained to 0.25 and 0.36 mm s^{-1} for the transmission integral.

3. Results and discussion

The spectra obtained at the two temperatures are shown in Fig. 1. The bottom part of the figure displays the spectrum recorded at 4.2 K. At this temperature

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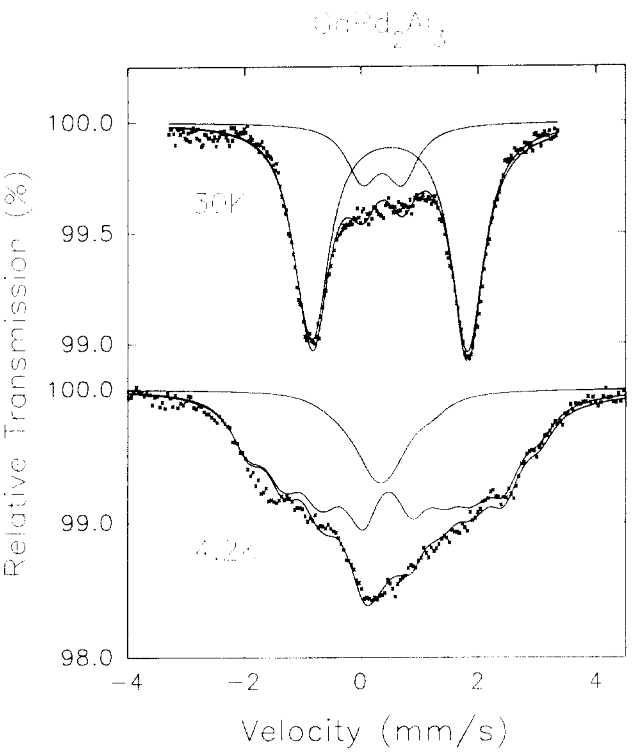

Fig. 1. ^{155}Gd Mössbauer spectra of $GdPd_2Al_3$ at 30 K (top) and at 4.2 K (bottom).

Table 1
Hyperfine parameters derived from fitting of the Gd Mössbauer spectra of $GdPd_2Al_3$

T (K)	V_{zz} (10^{21} V m^{-2})	$\mu_0 H_{eff}$ (T)	θ (deg)	IS (mm s^{-1})	f (%)
4.2	+12.6	26.0	49	0.48	81
	3.2	12.0	90	0.36	19
30	+12.6	0	–	0.48	81
	3.2	0	–	0.36	19

the compound is magnetically ordered and the spectrum shows Zeeman as well as quadrupolar splitting. The lower part of the figure refers to the paramagnetic regime, and the spectrum is quadrupole split only. The hyperfine parameters derived from fitting the two spectra are listed in Table 1. In both cases it was not possible to fit the data with a single spectrum. The presence of a second subspectrum had to be assumed, the relative intensity of which is about 19%.

The intensity of the latter subspectrum is substantially larger than to be attributable to the negligibly small amounts of the impurity phase detected by X-ray diffraction, and its presence therefore needs further discussion. The $PrNi_2Al_3$ structure adopted by the compound $GdPd_2Al_3$ is derived from the well-known $CaCu_5$ structure in which the 2c site is occupied by Pd atoms and the 3g site by Al atoms. However, this preferred site occupation may not be a very strict one, and site exchange between Pd and Al atoms may occur to some extent. Neutron diffraction experiments made on a single crystal of the isostructural compound $CePd_2Al_3$ showed that this site exchange should be very small because it was not detected in these experiments [6]. We have used a binomial distribution function to calculate the degree of site exchange needed to produce 19% of Gd atoms having a disturbed nearest neighbour shell. These calculations show that a site exchange of only 4% is required to give rise to a second Gd subspectrum of the observed intensity. Such a low degree of site exchange may be difficult to detect by careful analysis of neutron diffraction intensities. The same type of calculations shows that the site exchange mentioned leads to a disturbed nearest neighbour shell of (16 + 4)% of the Al atoms. In ^{27}Al NQR experiments made on powdered $CePd_2Al_3$ two broadened resonance lines of an approximate intensity ratio 1:4 were found [9]. These broadened lines may correspond to Al atoms having different nearest neighbour shells, indeed.

From the hyperfine parameters listed in the table for the main spectrum it can be inferred that the nuclear sites of Gd atoms with the ideal nearest neighbour configuration corresponding to the $PrNi_2Al_3$ structure experience a relatively strong electric field gradient. The value listed can be used to obtain information on the field gradient experienced at the site of the 4f electrons or equivalently, information on the second-order crystal field parameter A_2^0.

Band structure calculations made for several types of rare earth intermetallics showed that the electric field gradient is primarily determined by the asphericity of the on-site valence electron charge clouds of the Gd atoms [3]. These results made it also clear that the commonly assumed relation of the form $A_2^0 = -eV_{zz}(1-\sigma_2)/4(1-\gamma_\infty)$ lacks a fundamental basis because core excitations and the concomitant Sternheimer antishielding play only a minor role in determining the electric field gradient at the nuclear site [3]. The difference between A_2^0 and V_{zz} results from the fact that the on-site 5d electron charge cloud asphericity, determining mainly the former, and the on-site 6p charge cloud asphericity mainly responsible for the latter, need not be the same.

However, strong indications exist, based on computational results [1] as well as on experimental results [3], that there is still a relation between A_2^0 and V_{zz}. In a previous investigation [3] we used the change in magnitude and sign of A_2^0 in compounds of the series $RGa_{2-x}Al_x$ (observed by means of inelastic neutron scattering and measurements of the specific heat and magnetic properties on single crystals [10]) to determine the proportionality constant (in the semi-empirical relation $A_2^0[Ka_0^{-2}] = -\omega V_{zz}[10^{21}\ V\ \mathrm{m}^{-2}]$, employing the fact that a similar change in sign and magnitude was found for V_{zz} from Gd Mössbauer spectroscopy. With the value $V_{zz} = +12.6$ listed in Table 1 and $\varpi = 35$ obtained previously we find $A_2^0 = -440Ka_0^{-2}$.

The implications of this result are the following. For the case of $CePd_2Al_3$ we calculate $B_2^0 = \alpha_J\langle r^2\rangle A_2^0 = +31.1$ K. If the second-order crystal field term predominates, this means that the $|\pm 1/2\rangle$ state is the ground state, the overall crystal field splitting being 542 K. It should be realized, however, that the quadrupole spitting in Gd Mössbauer spectroscopy exclusively probes the second order parameter A_2^0 and provides no information on sign and magnitude of other crystal field parameters. Qualitatively our results are in concordance with results obtained by Mentink et al. on the basis of inelastic neutron scattering and specific heat measurements [6,11]. Our data can be regarded as additional proof of a crystal field split level scheme in $CePd_2Al_3$ with $|\pm 1/2\rangle$ as the ground state.

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