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Magnetic properties of GdPdSb and GdNiSb studied by ^{155}Gd-Mössbauer spectroscopy

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ABSTRACT

^{155}Gd-Mössbauer spectroscopy was applied to study the magnetic properties of GdPdSb with hexagonal LiGaGe structure and of GdNiSb in the cubic MgAgAs-type structure as well as in the hexagonal AlB_2-type structure. In GdPdSb magnetic ordering is observed at 13.0 K with indications of a tilted spin structure at lower temperatures. In the cubic phase of GdNiSb magnetic ordering is observed at 9.5 K and in the hexagonal phase around 3.5 K. These results are discussed in conjunction with previous investigations of these samples.

1. Introduction

Intermetallic compounds of LnMX type, where Ln is a lanthanide element, M is a transition metal and X is an sp element, have been studied intensively in recent years because of a large variety of structural, electronic and magnetic properties [1–3]. Here we studied the magnetic properties GdPdSb and GdNiSb, investigated previously with other methods [3–5], with ^{155}Gd-(86.5 keV)-Mössbauer spectroscopy.

2. Experimental

The preparation of the GdPdSb sample is described in Ref. [3], where the structural, electronic and magnetic properties were studied by a variety of methods, including band structure calculations. The derived lattice parameters of the hexagonal LiGaGe structure are in good agreement with the ones derived recently from single-crystals of GdPdSb [6]. As known from literature, GdNiSb may exhibit two different phases, a high-temperature phase with hexagonal AlB_2-type structure and a low-temperature phase with cubic MgAgAs-type structure [4,5]. The present GdNiSb sample contained both phases, as indicated by the XRD pattern and by the Mössbauer spectra shown below. Details of the sample preparation may be found elsewhere [7].

The ^{155}Gd-Mössbauer spectra were acquired using a ^{155}Eu:$SmPd_3$ source, which was moved sinusoidally at the same temperature as the absorber. The Mössbauer spectra were recorded in a He bath cryostat in the temperature range 1.8–48 K, the temperature of the absorber was monitored by a Si diode and kept constant within 0.1 K by a LakeShore cryogenic controller. The ^{155}Gd-spectra were analysed by a fit program which provided a full diagonalization of the mixed electric-quadrupole/magnetic-dipole interaction. This program uses the transmission integral, including the dispersion term for the E1 transition of ^{155}Gd, and enables also a multi-spectra fit of a temperature-dependent series of spectra monitoring a magnetic ordering, applied successfully in previous ^{155}Gd-Mösssbauer studies of complex magnetic structures [8].

3. Results and discussion

Typical ^{155}Gd-Mössbauer spectra, recorded at various low temperatures, are shown for GdPdSb and GdNiSb in Figs. 1 and 2, respectively. The spectra of GdPdSb, measured between 1.85 and 30 K, indicate below 13 K magnetic ordering, while they exhibit above 13 K an unresolved quadrupole splitting. From a simultaneous fit of seven spectra between 14 K and 30 K, an isomer shift $S = 0.468(4)$ mm/s with respect to the ^{155}Eu:$SmPd_3$ source and an electric field gradient of $V_{zz} = \pm 1.65(25) \times 10^{21}$ V/m^2 was derived. The latter value corresponds to a relatively small quadrupole splitting, $\Delta E_Q = \pm 0.43$ mm/s, of the $I = 3/2$ ground state of the ^{155}Gd-resonance. Therefore, the sign of V_{zz} could not be derived unambiguously from the spectra with mixed

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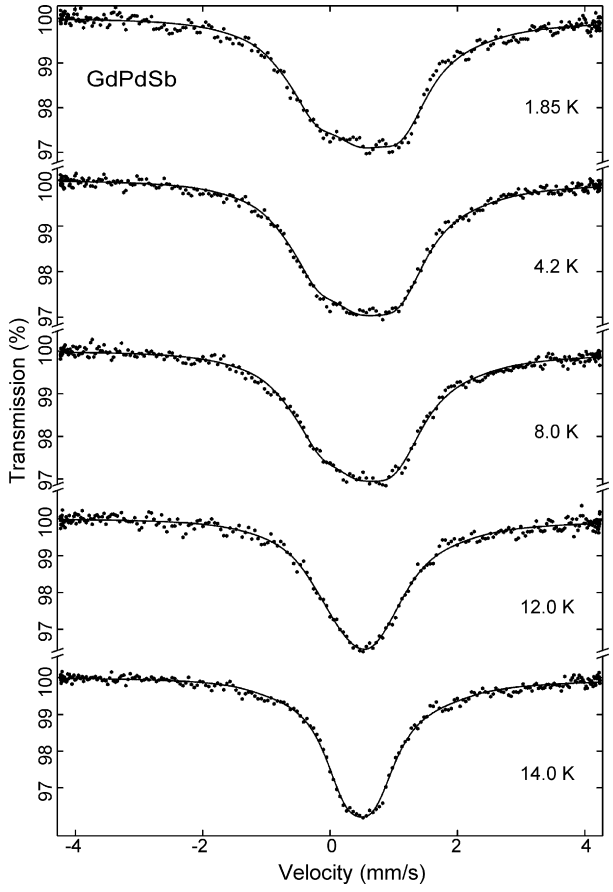

Fig. 1. Selected ^{155}Gd-Mössbauer spectra of GdPdSb at various temperatures (for details of the fit, see text).

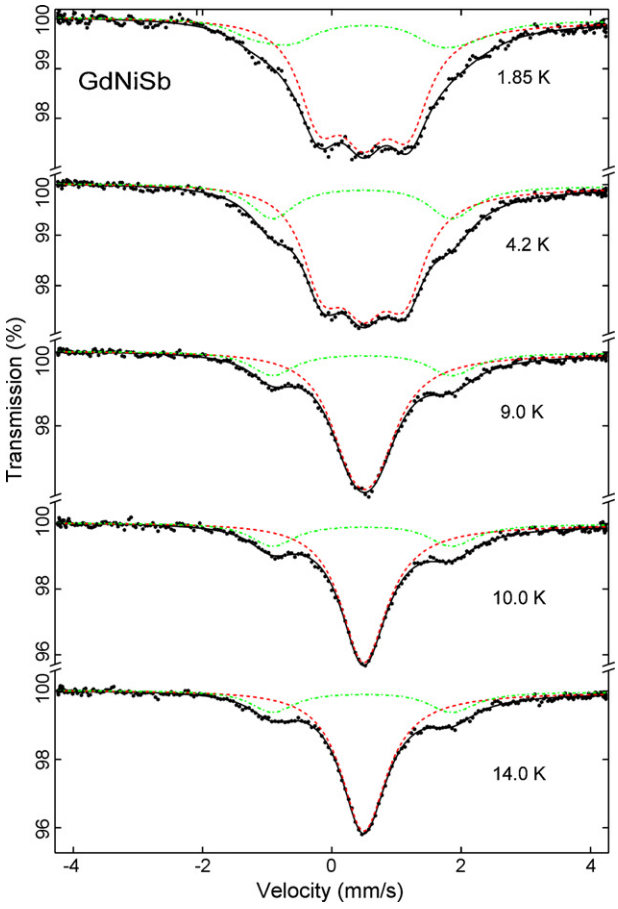

Fig. 2. Selected ^{155}Gd-Mössbauer spectra of GdNiSb at various temperatures. The dominant cubic phase (dashed line, red) is fitted at 10 K and higher temperatures by a single line and exhibits magnetic splitting in the spectra below 10 K. The hexagonal minority phase (dashed-dotted line, green) is fitted by a quadrupole doublet, which exhibits magnetic broadening in the spectrum at 1.85 K (see text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

electric-quadrupole/magnetic-dipole interaction at low temperatures, as done in previous ^{155}Gd-Mössbauer studies of Gd compounds with larger quadrupole splittings [8,9], and the spectra below 13 K were analysed therefore with a fixed value for the isomer shift and fixed positive and negative values of V_{zz} as given above (there is no significant temperature dependence for both the isomer shift and the quadrupole splitting to be expected at this low temperature range). Fig. 3 shows the derived hyperfine fields for a positive value of V_{zz}, from which a magnetic ordering temperature of 13.0(3) K was derived. It should be mentioned that a positive value of $V_{zz} = +1.0 \times 10^{21}$ V/m^2 was obtained also by self-consistent band structure calculations using the full potential linear augmented plane wave (FLAPW) method [10]. This method was already successfully applied in previous Mössbauer investigations of *RE* intermetallics [11]. A positive sign of V_{zz} can be derived also from the positive sign of the B_2^0 CEF parameter, observed in isostructural CePdSb for the Ce site [12]. The present magnetic ordering temperature is in excellent agreement with $T_N = 13.1(3)$ K, derived in the previous magnetic investigation of GdPdSb of the same sample studied here [3]. These values of T_N are, however, systematically lower than the ones reported previously for GdPdSb with $T_N = 15.5$ K [12], $T_N = 16.5$ K [13], and $T_N = 17$ K [14]. These small differences are possibly due to relative large external fields applied in the magnetisation measurements [13,14] and/or due to the fact that GdPdSb samples with hexagonal LiGaGe structure may exhibit different degrees in crystalline order of the Pd and Sb neighbours, evidenced here in a broadened linewidth in the ^{155}Gd-spectra (see below). It should be mentioned that GdPdSb was initially attributed to the

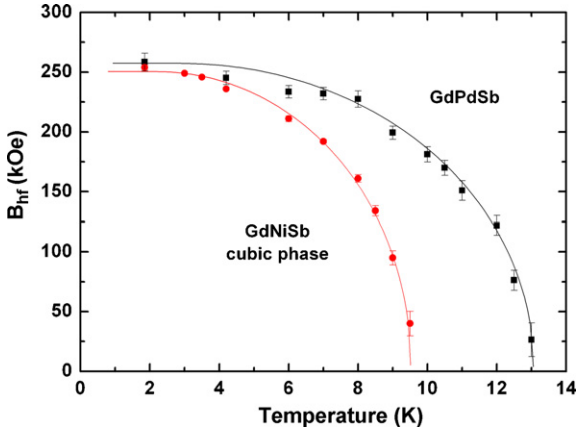

Fig. 3. Temperature dependence of the magnetic hyperfine fields B_{hf} at the Gd sites in GdPdSb (full circles, red) and in the cubic phase of GdNiSb (full squares, black). The Brillouin-like lines, indicating the magnetic ordering temperatures, are guides to the eye. The values of B_{hf} for GdPdSb were derived with fixed values of $V_{zz} = +1.65 \times 10^{21}$ V/m^2 and $\beta = 32^\circ$ (see text). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

hexagonal $CaIn_2$-type structure with a random distribution of Pd and Sb neighbours on the In sites [12–14].

An important information from the fits of the Mössbauer spectra of GdPdSb below T_N is delivered by the value of β, the angle between B_{hf}, the magnetic hyperfine field, and V_{zz}, the main axis of the electric field gradient. Since V_{zz} at the Gd ions is oriented parallel to the hexagonal *c*-axis due to the local symmetry, the angle β indicates the orientation of the ordered Gd moments with respect to the *c*-axis. For a positive sign of V_{zz}, we derive below 9 K a value of $\beta = 32(6)^\circ$. This observation could be explained by a ferromagnetic component, connected with a pronounced hysteresis as observed in the magnetisation measurements below 8 K [3], attributed to a canting of the Gd moments out of an initially anti-ferromagnetic arrangement. It should be mentioned that we derive for a negative value of V_{zz} a value of $\beta = 90(2)^\circ$. A final decision about the sign of V_{zz} and, correspondingly, about the value of β and the arrangement of the Gd moments, must await for further theoretical calculations of possible magnetically ordered Gd spin structures and further ^{155}Gd-Mössbauer studies, e.g. from single crystalline samples [6].

The ^{155}Gd-Mössbauer spectra of the GdNiSb sample (Fig. 2) demonstrate immediately the presence of two different phases, as indicated already in the XRD pattern. The dominant one with cubic MgAgAs-type structure can be unambiguously attributed to the unsplit resonance line in the spectra at 10 K and higher temperatures. The minority phase with hexagonal AlB_2-type structure is monitored by a quadrupole doublet with a large value of $V_{zz} = \pm 10.7(5) \times 10^{21}$ V/m^2 and a relative intensity of 25(1)% with respect to the cubic phase. The analysis of the spectra below 10 K reveal a magnetic splitting of the cubic site, as evidenced by the well resolved symmetric magnetic splitting at low temperatures. From the variation of the magnetic hyperfine field B_{hf}(T), magnetic ordering at $T_m = 9.5(3)$ K is derived (see Fig. 3). This value is in sharp contrast to a previous study of GdNiSb, reporting from resistivity measurements for the cubic phase $T_N = 3.7$ K [4]. The hexagonal phase of GdNiSb, characterised by the large quadrupole splitting, shows the onset of magnetic ordering around 3.5 K, in accordance with the previous study, reporting $T_N = 3.3$ K for the hexagonal phase [4]. The fit analysis of this minority phase in the spectra below 4.2 K is strongly hampered by the spectral overlap with the magnetically split cubic phase. Best fits were obtained with a negative value of V_{zz} (in agreement with theoretical calculations as described above) and with $\beta = 90^\circ$, yielding values for the magnetic hyperfine field B_{hf} of 120(30) kG and 60(20) kG at 1.85 K and 3.0 K, respectively. Future ^{155}Gd-studies on GdNiSb samples with the hexagonal as majority phase [7] will deliver more information on the magnetic properties of this phase. It is, at present, of interest that the observed isomer shifts are very similar, $S = 0.484(4)$ mm/s and 0.460(6) mm/s for the cubic and hexagonal phase of GdNiSb, respectively, and compare well with $S = 0.468(4)$ mm/s reported above for hexagonal GdPdSb. The observed absorber linewidths, $\Gamma_a = 0.40$ mm/s and 0.50 mm/s for the cubic and hexagonal phase of GdNiSb, respectively, and $\Gamma_a = 0.56$ mm/s for GdPdSb point to some structural disorder in both hexagonal phases, observed also in the ^{155}Gd-spectra of an other ternary Gd intermetallic [15]. Finally it should be noted that the local binding strength at the Gd sites in GdNiSb is stronger in the hexagonal phase than in the cubic phase as derived from ^{155}Gd-spectra measured up to 48 K.

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