ELSEVIER
Journal of Alloys and Compounds 262–263 (1997) 108–113
Journal of ALLOYS AND COMPOUNDS

Crystal and magnetic properties of GdTSn compounds (T = Ag, Au)

K. Łątka[a,*], E.A. Görlich[a], W. Chajec[a], R. Kmieć[b], A.W.J. Pacyna[b]

[a] *M. Smoluchowski Institute of Physics, Jagiellonian University, Reymonta 4, 30-059 Kraków, Poland*
[b] *H. Niewodniczański Institute of Nuclear Physics, Radzikowskiego 152, 31-342 Kraków, Poland*

Abstract

The results of structure, ac and dc susceptibilities, and ^{119}Sn Mössbauer studies of GdAgSn and GdAuSn compounds are presented. It was found that these compounds order anti-ferromagnetically at $T_N = 34.3(2)$ K, and $T_N = 22.9(2)$ K, respectively. Additionally a second transition at $T_f = 15.3(2)$ K was discovered for both intermetallics. The nature of this second transition is discussed and strong experimental arguments supporting the spin-glass origin and reentrant antiferromagnetic character of the compounds under study are given. © 1997 Elsevier Science S.A.

Keywords: Mössbauer studies; X-ray; ac/dc susceptibility; Aniferromagnetism; Spin glass; Re-entrant transitions; Magnetic hyperfine field distribution; Gadolinium

1. Introduction

The GdTSn compounds (T = Ag, Au) belong to a rich class of ternary RTSn intermetallics with R a rare-earth element or an actinide and T a transition element (3d, 4d or 5d). The RTSn compounds form a variety of crystal and magnetic structures [1]. Their magnetic ordering is mostly anti-ferromagnetic, but ferromagnetic ordering also takes place. Previous investigations show that the GdTSn compounds crystallize in the hexagonal $CaIn_2$ type of structure with space group $P6_3/mmc$ [2,3]. This structure consists of Gd and T–Sn layers alternating along the c-axis, and possible crystallographic disorder, allowed by this structure within T–Sn positions, can influence many physical properties. Recently, a series of RAgSn (R = Nd, Tb, Ho) compounds was characterized by neutron diffraction measurements [4] and the authors claimed that these stannides adopted the hexagonal GaGeLi-type structure (space group $P6_3mc$), an ordered derivative of the $CaIn_2$ type. However, the choice between these two structure types in the case of powder diffraction experiments is usually ambiguous [5,6]. The Gd compounds are especially well suited for magnetic investigations, since the trivalent Gd is in the $^8S_{7/2}$ state and no significant crystal field effects are expected thus making theoretical interpretation of the experimental results more straightforward. The local sensitivity of the diamagnetic ^{119}Sn Mössbauer probes gives the unique possibility of following the temperature evolution of hyperfine parameters which may be influenced by structural and magnetic phase transformations. In recent studies [7,8] some structural properties of RTSn compounds were discussed thoroughly.

In the present work, we have carried out measurements of the temperature dependence of the magnetic susceptibility and ^{119}Sn Mössbauer spectroscopy in GdAgSn and GdAuSn compounds for good quality samples since the properties of these compounds are known to be very sensitive to heat treatment.

---

[*] Corresponding author.

PII S0925-8388(97)00338-1

2. Experimental

The polycrystalline intermetallic compounds GdAgSn, and GdAuSn, were prepared by melting appropriate amounts of the constituents in an arc furnace under purified argon atmosphere. The samples were then wrapped into tantalum foil and subsequently annealed in evacuated silica tubes at 500° for 1 week. The preparation technique was essentially the same as that of RAuSn series, which had been described previously in Mazzone et al. [2] and Marazza et al. [3]. The room temperature powder X-ray measurements were obtained with a Siemens D-501 diffractometer using the Ni-filtered CuK_α radiation. The bulk magnetic dc and ac susceptibility (ACS) measurements were carried out using Lake Shore susceptometer (Series 7225) in the temperature range 4.2–200 K. The in-phase $\chi'(\omega)$ and out of phase $\chi''(\omega)$ components were recorded simultaneously as a function of temperature with internal frequencies ranging from 20 Hz to 1000 Hz and the amplitude H_{ac} of the applied oscillating field was changed from 0.5 Oe up to 10 Oe for individual frequencies kept constant at a given temperature point. The zero field ACS measurements were made by cooling a sample in zero field from room temperature down to 4.2 K. After zero field cooling an external magnetic field was switched on and the field dependence of ACS was registered with rising temperature for magnetic fields up to 1500 Oe for different frequencies and amplitudes of H_{ac}.

The ^{119}Sn Mössbauer investigations were performed using a conventional constant-acceleration spectrometer of Kankeleit type in transmission geometry. A Ba^{119}SnO$_3$ source was kept at temperatures close to 4.2 K and series of ^{119}Sn Mössbauer spectra were recorded at temperatures in the range of 4.2 K–50 K. Absorbers were made of the powdered compounds with optimal thickness of 38 mg cm^{-2} and 26 mg cm^{-2} for GdAgSn, and GdAuSn samples, respectively. A palladium foil of 0.05 mm thickness was used as a critical absorber for tin X-rays. The shapes of the spectra were analysed by least-squares fits within the Lorentz approximation. To calculate the resonance-line positions and their relative intensities, the numerical diagonalization procedure of the hyperfine interaction Hamiltonian H_{hf} was used. The full analysis leads to data for the isomer shift δ_{is}, the quadrupole interaction constant: $\Delta E_Q = eQV_{zz}/4$, the magnetic hyperfine field H_{hf} and for the polar angle θ, that is, for the direction of the magnetic hyperfine field with respect to the z-axis of the EFG (electric field gradient) tensor. To account for an observed broadening of the low temperature spectra of GdAuSn compound caused by possible distribution in magnitudes of the hyperfine magnetic field H_{hf} an extended approach first presented by Czjzek and Berger [9] was applied. Apart from the average value $\langle H_{hf} \rangle$ and the second moment of the field distribution $\delta_H = (\langle H_{hf}^2 \rangle - \langle H_{hf} \rangle^2)^{1/2}$, also the average value $\langle \theta \rangle$ and its second moment of the distribution $\delta_\theta = (\langle \theta^2 \rangle - \langle \theta \rangle^2)^{1/2}$, were fitted as independent parameters. All spectra can be reproduced satisfactorily in this way.

3. Results

X-ray diffraction patterns revealed only single phase for both compounds. The structure was confirmed to be hexagonal CaIn$_2$-type with space group P6$_3$/mmc [2,3] and lattice constants are given in Table 1. The results of dc susceptibility data (collected in Table 1) showed that both compounds order antiferromagnetically. The susceptibilities above T_N could be fitted with the Curie–Weiss law, yielding negative paramagnetic Curie temperatures for both compounds and magnetic effective moments which are close to the theoretical value 7.94 μ_B for Gd^{3+} ion (Table 1). The T_N value obtained for GdAgSn equal to 34.3 (2) K agrees very well with that which can be estimated using Fig. 1 (presented in Ref. [10]). For GdAuSn $T_N = 22.9(2)$ is much lower than that reported in Bialic et al. [8] $T_N = 35$ K [11] and also differs from $T_N = 28.6$ which results from the Brillouin curve fitted to the H_{hf} data shown in Fig. 5 of Ref. [8]. This is probably due to the different heat treatment procedures applied. For example the sample used in the latter reference was annealed at 800°C in comparison to 500°C in our case. Low field dc magnetic measurements (taken at $H = 100$ Oe) showed that both materials undergo another transition at almost the same temperature T_f equal to 15.3(2) K. To elucidate the character of this transition ACS measurements were undertaken. Very good agreement of the results derived for transition temperatures and effective magnetic moments using ac and dc techniques was obtained. The temperature dependencies of the real and the imaginary part of the $\chi(\omega)$ presented in Figs. 1 and 2 for different frequencies confirm that two transitions take place for GdAgSn and GdAuSn compounds, respectively. In case of the latter compound, one can observe a smaller effect of frequency on the susceptibility behaviour. Fig. 3 illustrates the influence of external magnetic fields up to 1500 Oe on $\chi'(\omega)$ and $\chi''(\omega)$ components for GdAgSn, and it is clearly seen that increasing the strength of an external magnetic field has no influence on the first high temperature transition localised at T_N while the second transition at 15.3 K is washed out. This observation together with remarkable influence of frequency on the $\chi'(\omega)$ and $\chi''(\omega)$ amplitudes (see Figs. 1 and 2) gives a hint that this transition can be related to the spin-glass (SG) state.

Indeed, the field-cooled (FC) dc-experiment performed for GdAuSn in the field $H_0 = 500$ Oe showed a saturation effect of FC-susceptibility with decreasing temperature which is a characteristic feature of SG behaviour. ^{119}Sn Mössbauer spectra of GdAgSn are presented in Fig. 4. Owing to the non-cubic local symmetry of the Sn sites the spectra measured above T_N present typical quadrupole doublets and they are well fitted without any impurity component. Low temperature spectra obtained around and below T_N for GdAgSn can be well fitted assuming two magnetic components with different magnetic hyperfine fields, similar to the case of GdCuSn [8,12]. The observed broadening of the resonance line for both components at 4.2 K in comparison to the value obtained at 40 K, i.e. above T_N (Tables 2 and 3) point to a certain distribution of the magnetic hyperfine fields. The temperature dependence of the relative fractions for these two magnetic components is presented in Fig. 5. It is evident that the fraction of the component 2 (see Table 3) with a smaller value of magnetic hyperfine field increases with temperature while the relative contribution of the component 1 (being largest at 4.2 K) decreases at the same time. On the other hand, one component taking into account the proper distribution of magnetic hyperfine fields is enough to get satisfactory fits for magnetically split GdAuSn spectra without any trace of non-magnetic component which was observed in [8] for this compound (but for a different sample) below T_N. The derived hyperfine interaction parameters above T_N and at 4.2 K for both compounds are shown in Tables 2–4. In spite of possible sample differences the results obtained for the gold compound studied in this work agree quite well with those obtained previously [8]. It is worth noting the rather good agreement between the Néel temperatures derived from magnetic measurements with those resulting from ^{119}Sn Mössbauer investigations (see Fig. 6) although small but non-zero local magnetic hyperfine fields survive over T_N owing to short-range order effects. Simultaneously, no drastic change can be registered in the shape of ^{119}Sn Mössbauer spectra and consequently in the temperature dependencies of magnetic hyperfine fields close to the second transition at the temperature T_t (Fig. 6).

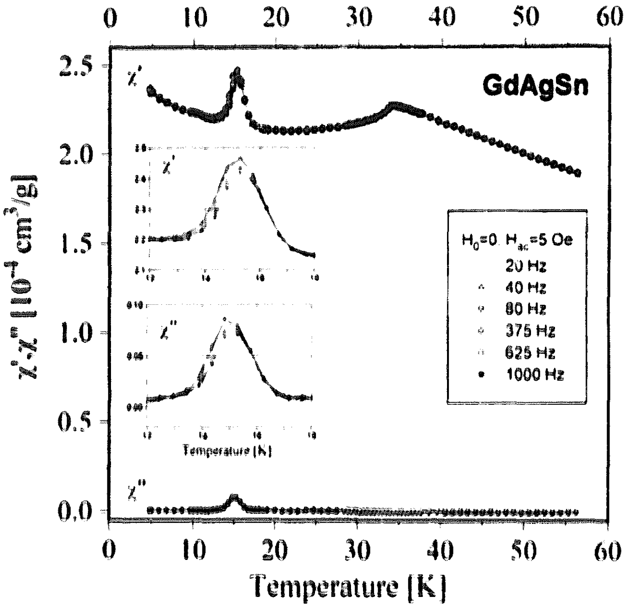

Fig. 1. Zero-field susceptibilities $\chi'(\omega)$ and $\chi''(\omega)$ for GdAgSn recorded simultaneously as a function of temperature with internal frequencies ranging from 20 Hz to 1000 Hz.

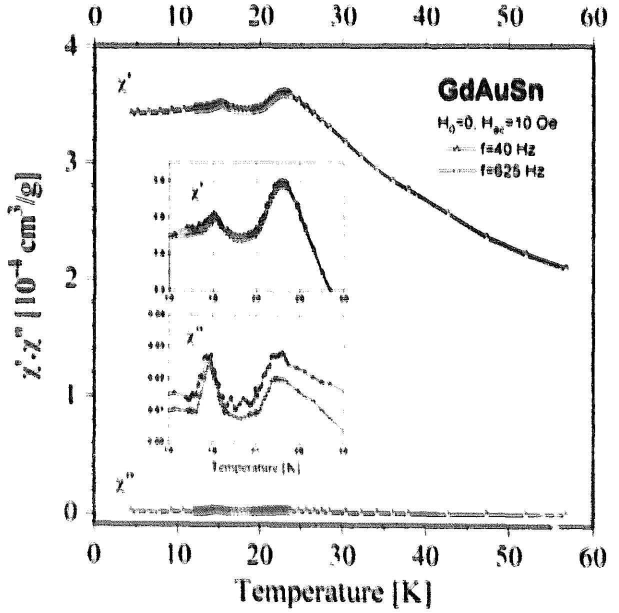

Fig. 2. Zero-field susceptibilities $\chi'(\omega)$ and $\chi''(\omega)$ for GdAuSn recorded simultaneously as a function of temperature at two internal frequencies 40 and 625 Hz.

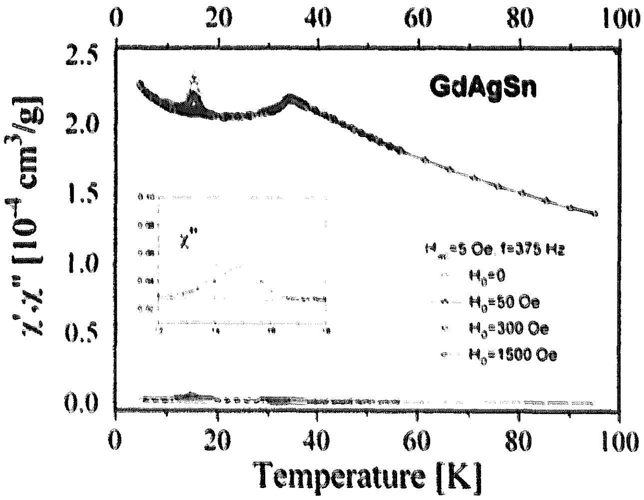

Fig. 3. Temperature dependence of $\chi'(\omega)$ and $\chi''(\omega)$ susceptibilities for GdAgSn measured after zero-field cooling at different magnetic fields up to 1500 Oe at the constant frequency, $f = 375$ Hz.

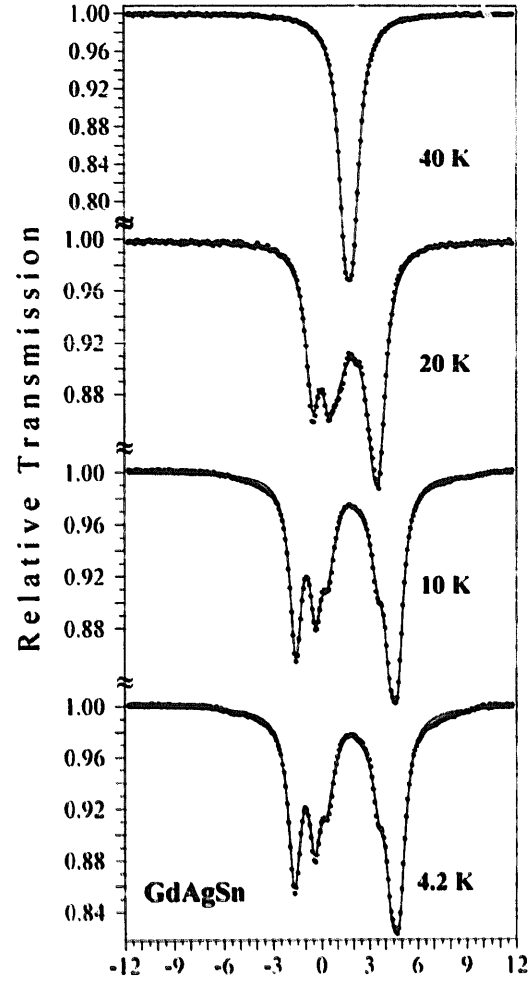

Fig. 4. ^{119}Sn resonance spectra for GdAgSn sample obtained at various temperatures above and below T_N. The continuous lines represent the least-squares fit to the experimental points.

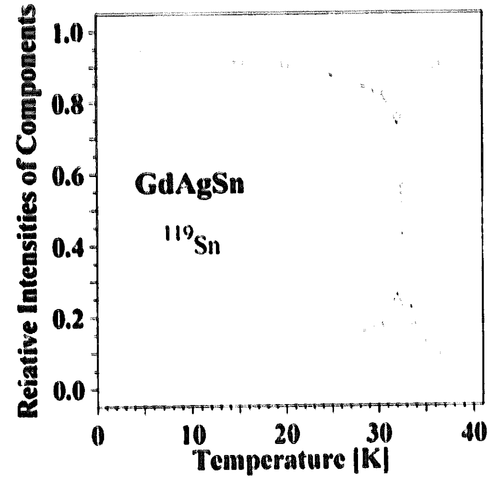

Fig. 5. Relative intensities of the two magnetic components observed for GdAgSn compound derived from fits presented in Fig. 4. For details see the text.

4. Discussion

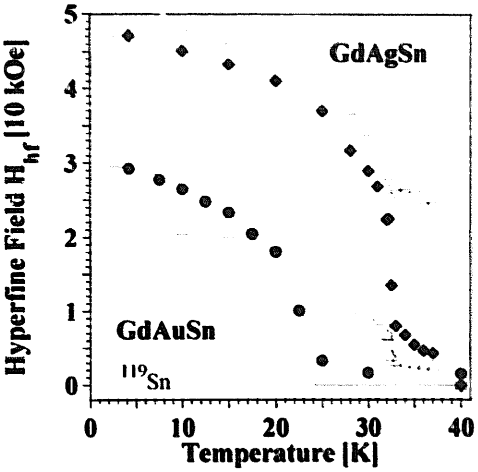

Fig. 6. Temperature dependence of the magnetic hyperfine field at the Sn sites for GdAgSn (triangles) and GdAuSn (solid circles). The continuous line represents the least-squares fit of the Brillouin function for S = 7/2 for the average values of magnetic hyperfine fields, $\langle H_{hf} \rangle$.

In the following discussion we will mainly focus our attention on magnetic properties associated with the existence of the second magnetic transition discovered for both compounds studied by ACS measurements. Since exhaustive treatment of the magnetic structure of GdTSn (where T = Cu, Au) compounds was recently carried out in Bialic et al. [8] we adopt some conclusions which were derived there to our analysis.

We begin with a statement that two important factors for formation of the SG state, e.g. *randomness* and *frustration* [13] can be met for the compounds studied. Random distribution of the noble atoms and tin atoms over In sites in the $CaIn_2$ structure leads to a variety of local environments for a given atom in the crystal lattice which in turn influences mutual mag-

Table 1
Crystal and magnetic data for Gd*T*Sn (*T* = Ag, Au) compounds

Compound	a [Å]	c [Å]	T_N (K)	T_f (K)	θ_p (K)	μ_{eff} (μ_B)
GdAgSn	4.709(1)	7.425(3)	34.3(2)	15.3(2)	−54(1)	8.01(2)
GdAuSn	4.657(1)	7.433(2)	22.9(2)	15.3(2)	−29(3)	7.61(31)

Table 2
The hyperfine interaction parameters inferred from the ^{119}Sn resonance spectra of the GdTSn intermetallic compounds above the Néel temperatures

Compound	T (K)	$\lvert\Delta E_Q\rvert$ [a] (mm s^{-1})	δ_{IS} [b] (mm s^{-1})	Γ_A [c] (mm s^{-1})
GdAgSn	40	0.26(1)	1.76(1)	0.85(2)
GdAuSn.	40	0.31(1)	1.74(1)	0.74(2)

[a] $\Delta E_Q = eQV_{zz}/4$.
[b] δ_{IS} is relative to the $Ba^{119m}SnO_3$ source.
[c] Half-width of the resonance line.
For E_γ = 23.875 keV gamma transition in ^{119}Sn: 1 mm s^{-1} corresponds to $7.963(2) \times 10^{-8}$ eV or 19.253(6) MHz.

Table 3
The hyperfine interaction parameters inferred from the ^{119}Sn resonance spectra of the GdAgSn intermetallic compound at $T = 4.2$ K

Compound GdAgSn	H_{hf}(kOe)	ΔE_Q^a (mm s^{-1})	δ_{is}^b (mm s^{-1})	θ (°)	Γ^d (mm^{-1}s)
Component 1	48.7 (2)	−0.260$^{(c)}$	1.75 (1)	21 (1)	0.92 (2)
Component 2	21.9 (4)	−0.260$^{(c)}$	1.75 (1)	91 (2)	0.92 (2)

Table 4
The hyperfine interaction parameters inferred from the ^{119}Sn resonance spectra of the GdAuSn intermetallic compound at $T = 4.2$ K

Compound GdAuSn						
$\langle H_{hf} \rangle$ (kOe)	ΔE_Q^a (mm s^{-1})	δ_{is}^b (mm s^{-1})	$\langle \theta \rangle$ (°)	Γ^d (mm s^{-1})	δ_H^c (kOe)	δ_θ^c (°)
29.2(2)	−0.31$^{(c)}$	1.67(1)	32(1)	1.04(1)	6.1(1)	15(1)

[a] $\Delta E_Q = eQV_{zz}/4$.
[b] δ_{is} is relative to the Ba^{119m}SnO$_3$ source.
[c] Parameters kept constant during the fit equal to the respective values obtained above T_N.
[d] Half-width of the resonance line.
[e] $\delta_H = (\langle H_{hf}^2 \rangle - \langle H_{hf} \rangle^2)^{1/2}$; $\delta_\theta = (\langle \theta^2 \rangle - \langle \theta \rangle^2)^{1/2}$.
For $E_\gamma = 23.875$ keV gamma transition in ^{119}Sn: 1 mm s^{-1} corresponds to $7.963(2) \times 10^{-8}$ eV or 19.253(6) MHz.

netic interactions of Gd magnetic moments and which is the main reason for the observed distribution of magnetic fields at the tin site revealed in this work by ^{119}Sn Mössbauer spectroscopy. On the other hand, frustration can be expected since competition of ferro- and anti-ferromagnetic interactions was fairly well confirmed for many RTX compounds [1] and this competition is an intrinsic feature also for GdTSn compounds [7,3] (see discussion) as the proposed magnetic structure consists of magnetic moments coupled ferromagnetically in chains along the c-axis and antiferromagnetically ordered within the plane. Such a structure is consistent with results obtained by ^{119}Sn Mössbauer spectroscopy. In fact, an SG state was discovered recently for UCuSi and UCuGe having the hexagonal CeCd$_2$ structure [14,15] and for NdCuSn possessing just the CaIn$_2$ structure [12]. However, one can underline that for reported UCuSi and for NdCuSn samples no indication of long range order was found down to 4.2 K while UCuGe is a reentrant ferromagnet and GdTSn (T = Ag, Au) compounds can be classified as reentrant antiferromagnets. Indeed, the lack of frequency effect on the T_N as well as the lack of frequency shift (Figs. 1 and 2) on T_f confirm the predominance of the nearest-neighbour antiferromagnetic interactions [16] in the latter compounds.

The considerable distribution of the magnetic hyperfine fields at the ^{119}Sn sites below magnetic transition temperatures, T_N, detected by Mössbauer spectroscopy persists down to the lowest experimental temperatures (see Results and Tables 3 and 4) and it is compatible with the SG state which is always associated with spin disordering. However, this distribution is much narrower than that found in UAuSn [17] which is due to much weaker *4f-(s,d)* hybridization effects in comparison to *5f-(s,d)* hybridization. The most striking feature of the results displayed in Table 4 is a large second moment of the $\langle \theta \rangle$ value given by δ_θ. This is a direct indication of spin disordering and in fact, supports the idea that we are dealing with local differences in the way of magnetic ordering characteristic for the SG state.

The temperature dependence of the average magnetic hyperfine field $\langle H_{hf} \rangle$ in the case of the GdAgSn compound deviates from $S_{7/2}$ Brillouin-functions (Fig. 6) indicating more complex magnetic interactions. The presence of two components with temperature dependent contributions proves that the Ag-compound is magnetically inhomogeneous. In particular, it reveals the microscopic mechanism of the demagnetization process when approaching T_N. As far as the SG transition is concerned at T_f it has no observable influence on hyperfine interactions of either component. The continuous behaviour of the magnetic hyperfine field vs. temperature around T_f (Fig. 6) is in favour of SG transition as the local spin arrangement is not significantly modified while the transition to another ordered magnetic structure is likely to result in a different hyperfine pattern.

The fact that transition temperatures T_f to the SG state are within the same experimental limits for both studied compounds seems to be not accidental owing to comparable lattice constants, spin concentrations and probably similar magnetic exchange interactions.

In contrast to known examples of SG states among amorphous Gd systems [18] the compounds studied here are crystallographically ordered substances. It is a common belief that in amorphous materials, the SG state can occur owing to competing near-neighbour interactions caused by randomly varying bond angles and interatomic spacings. Therefore the question arises as to what the driving mechanism for the SG state is in ordered materials. It seems that this problem is still open and needs further elucidation.

Acknowledgements

We would like to express our gratitude to Dr. Robert Kruk from H. Niewodniczański Institute of Nuclear Physics in Cracow, Poland for critical discussion, valuable comments and suggestions. This work was supported in part by State Committee for Scientific Research in Poland within Grant No 2 P03B 116 12.

References

[1] A. Szytuła, J. Leciejewicz, Handbook of Crystal Structures and Magnetic Properties of Rare Earth Intermetallics, Boca Raton, CRC Press, 1994.

[2] D. Mazzone, D. Rossi, R. Marazza, R. Ferro, J. Less-Common. Met. 80 (1981) P47.

[3] R. Marazza, D. Rossi, R. Ferro, J. Less-Common. Met. 75 (1980) P25.

[4] W. Bażela, M. Guillot, J. Leciejewicz, K. Maletka, A. Szytuła, Z. Tomkowicz, J. Mag. Mag. Mat. 140 (1995) 1137.

[5] W. Bażela, J. Leciejewicz, K. Małetka, A. Szytuła, J. Mag. Mag. Mat. 117 (1992) L1.

[6] M. Guillot, Z. Tomkowicz, Z. Zach, J. Alloys Comp. 226 (1995) 131.

[7] E.A. Görlich, K. Łątka, R. Kmieć, submitted to Physica B.

[8] D. Bialic, R. Kruk, R. Kmieć, K. Tomala, J. Alloys Comp. (1997) in the press.

[9] G. Czjzek, W.G. Berger, Phys. Rev. B 1 (1970) 957.

[10] A. Adam, J. Sakurai, Y. Yamaguchi, H. Fujiwara, K. Mibu, T. Shinjo, J. Mag. Mag. Mat. 90/91 (1990) 544.

[11] H. Oesterreicher, J. Less-Common Met. 55 (1977) 131.

[12] R. Hatzl, M. Reissner, M. Forsthuber, E. Gratz, W. Steiner, G. Wiesinger, K. Yvon, in: I. Ortalli (Ed.), Conference Proceedings 50 (ICAME-95) SIF, Bologna, 1996, 347-350.

[13] K. Binder, Y. Yang, Rev. Mod. Phys. 58 (1986) 801.

[14] V.H. Tran, R. Troć, J. Mag. Mag. Mat. 86 (1990) 231.

[15] V.H. Tran, A.J. Zaleski, R. Troć, P. de V. du Plessis, J. Mag. Mag. Mat. 162 (1996) 247.

[16] M. Hardiman, Bull. Am. Phys. Soc. 25 (1980) 176.

[17] R. Kruk, R. Kmieć, K. Łątka, K. Tomala, R. Troć, V.H. Tran, J. Alloys Comp. 232 (1996) L8.

[18] T. Mizoguchi, T.R. McGuire, S. Kirkpatrick, R.J. Gambino, Phys. Rev. Lett. 38 (1977) 89.