[119]Sn hyperfine interactions in REAuSn (RE = rare earth)

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Abstract. Intermetallic REAuSn (RE = rare earth elements) compounds were studied by means of X-ray diffraction (XRD), magnetic measurements and [119]Sn Mössbauer spectroscopy. It was shown that the majority of them exhibit complex antiferromagnetic ordering at low temperatures. The nature of hyperfine interactions has been discussed based on γ-ray absorption spectroscopy together with magnetic and structural data. Lanthanide contraction is reflected in the lattice parameters and isomer shifts. Strong experimental arguments support correlation between crystallographic type of structure and magnetic disordering in investigated compounds.

Introduction

In recent years we have investigated a series of equiatomic intermetallic REAuSn compounds (RE = rare earth elements) [2, 6–13]. These stannides belong to a large family of equiatomic ternary rare earth compounds, which adopt different crystal structures resulting in a large variety of physical properties [18]. These properties are related to the hybridization between the rare earth 4*f*-electron states and the conduction electron states.

The aim of this report is to review the results of our crystallographic and spectroscopic studies, systematically made for REAuSn series. Especially, [119]Sn Mössbauer spectroscopy, as a microscopic technique, was applied to characterise the local electronic properties of the compounds under investigation. By virtue of the local sensitivity of the Mössbauer probe it is possible to investigate the temperature evolution of hyperfine parameters following structural and magnetic phase transformations.

Experimental

The polycrystalline samples were synthesized by arc melting of the stoichiometric amounts of the constituent elements under overpressure of the purified argon atmosphere. Melting was performed several times to ensure a high homogeneity of the samples. The weight losses during melting procedure did not exceed 0.5%. Afterwards, the samples were wrapped into tantalum foil and subsequently annealed in an evacuated silica tube at 773 K for a week. Samples were examined by means of powder X-ray measurements at room tem-

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perature with a Siemens D-501 diffractometer with Ni-filtered CuK_α radiation. The standard FULLPROF computer package ([8] and references therein) was then used for lattice parameter calculations for all type of structures.

The magnetization and the magnetic susceptibility measurements were carried out on the powdered samples by means of the Faraday's method with a Cahn RG automatic electrobalance as well as using a Lake Shore 7225 AC susceptometer/DC magnetometer in the temperature range 4.2 K < T < 300 K. In the first case, the sample was placed in an inhomogeneous magnetic field with a constant value of $H_0 \cdot \partial H_0 / \partial z$, while in the latter one the used magnetic field H_0 was homogeneous ranging up to 57.5 kOe. Temperature dependences of the complex AC magnetic susceptibility $\chi = \chi' - i\chi''$ were measured at different driving field frequencies f and depending on the amplitude of this field H_{AC}. In addition, for better characterization of the samples, the higher harmonics were also investigated as a function of temperature.

The ^{119}Sn Mössbauer spectra were recorded at temperatures in the range 2.2–300 K with a conventional constant-acceleration spectrometer of the Kankeleit type in the transmission geometry. A palladium foil of 0.05 mm thickness was used as a critical absorber for tin X-rays to reduce the background intensity of the recorded spectra. During measurements, the temperature of the $Ba^{119m}SnO_3$ source was close to 4.2 K, while the temperature of the absorber was varied between 2.2 K and room temperature. The spectra were analyzed by means of least-squares fitting procedures using full hyperfine Hamiltonian within the Lorentz approximation. The resonance spectra showing distribution of the magnetic hyperfine fields were additionally analyzed employing the Wivel and Mørup method ([8] and references therein).

Results and discussion

Crystal structure

Depending on the size and the valence state of the rare earth element, the title compounds crystallize with different structure types. Compounds with RE = La-Nd adopt the hexagonal LiGaGe-type of structure [7, 11, 14], a ternary ordered variant of the $CaIn_2$-type, the latter one being preferred for RE = Sm, Gd-Dy [1, 6, 9, 12, 13]. For the smaller sized rare earth elements, like Tm and Lu, the REAuSn compounds adopt the cubic MgAgAs-type of structure [13, 17]. ErAuSn is dimorphic ([8, 10, 17] and references therein), whereas EuAuSn and YbAuSn crystallize in the complex superstructures of the orthorhombic KHg_2-type [3, 15]. In contrast to the results obtained in [16], only one crystallographic structure of $CaIn_2$-type appears for the HoAuSn sample [8], independently of the heat treatment procedure used.

It has been found that ErAuSn can be synthesized by application of a proper heat treatment in two polymorphic forms crystallizing in a high-temperature form of the hexagonal $CaIn_2$-type of structure (space
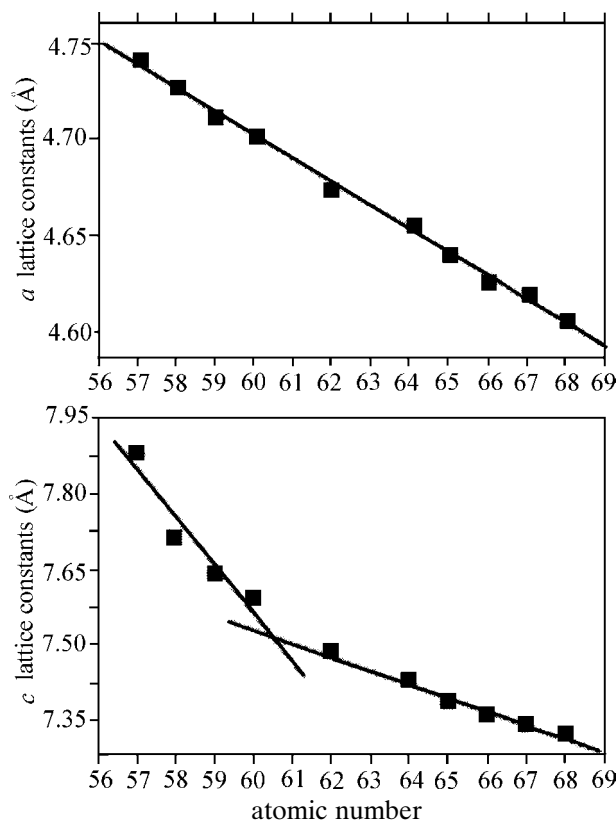

Fig. 1. Lattice parameters a and c as a function of RE atomic number.

group $P6_3/mmc$) and a low-temperature form of the cubic MgAgAs-type (space group $F\bar{4}3m$). This is in contrast to the previous studies where only cubic form was established ([10] and references therein).

For the equiatomic REAuSn compounds, we observed a linear correlation of the a-axis parameter with the RE-elemental number (see Fig. 1). This is a well known dependence called lanthanide contraction. Surprisingly, c-axis parameter does not reveal the same linear correlation as indicated by two straight guiding lines in Fig. 1, which contradicts the previous studies [16].

Magnetic properties

The majority of REAuSn compounds order antiferromagnetically at low temperatures showing complex structures due to interplay between magnetic interactions [1, 2, 6–15, 18] and crystal field effects [1–12, 14]. Only compounds with RE = La, Tm, Yb and Lu remain nonmagnetic down to very low temperatures [3, 7, 13, 17]. The critical temperatures (i.e. respective Néel T_N or Curie T_C temperatures) and other magnetic data are displayed in Table 1. Magnetic measurements revealed that the temperature dependences of magnetic susceptibility χ_σ obtained in paramagnetic region for all compounds presented in Table 1, except that with La, can be well fitted using the modified Curie-Weiss law in the form $\chi_\sigma = \chi_0 + C/(T - \Theta_P)$, where χ_0 is a temperature independent factor, C is the Curie constant and Θ_P is the paramagnetic Curie temperature. The

Table 1. Magnetic data for REAuSn compounds

Compound	Crystal and magnetic structure		χ_0 $(\times 10^{-6}\, cm^3/g)$	Θ_P (K)	μ_{eff} (exp.) (μ_B)	μ_{eff} (theor.) (μ_B)	T_N, T_C (K)	Ref.
LaAuSn	GaGeLi	NM				0	–	4
CeAuSn	GaGeLi	AF	–40.1	1.65	2.52	2.54	7.0 4.5	4
PrAuSn	GaGeLi	AF	–11.0	2.83	3.37	3.58	3.3 2.7	4
NdAuSn	GaGeLi	AF	1.8	–15.9	3.60	3.62	13.8 10.5	3, 7
SmAuSn	CaIn$_2$	AF				0.85	36.5*	6
GdAuSn	CaIn$_2$	spin glass		–29.0	7.61	7.94	22.9 15.3	1
TbAuSn	CaIn$_2$	AF	3.1	–27.0	9.33	9.72	14.0	9
DyAuSn	CaIn$_2$	AF	2.8	–16.3	10.36	10.65	7.3	8
HoAuSn	GaGeLi	AF	7.0	–7.7	10.46	10.60	8.7	5
ErAuSn	CaIn$_2$	AF		–8.7 –0.5	9.58 9.53	9.58	18.1 (cub) 12.1 (hex)	2
TmAuSn	MgAgAs	NM	10.0	–6.6	8.11	7.56	–	9

* Mössbauer data.   NM – nonmagnetic.   AF – antiferromagnetic.

experimental effective magnetic moments μ_{eff}(exp.) deduced from the fitted Curie constants C are fairly well comparable to the theoretical values μ_{eff}(theor.) characteristic of the respective free RE^{3+} ions (see Table 1).

Applying very precise AC and DC magnetic measurements, additional magnetic phase transitions in light REAuSn (RE = Ce, Pr, Nd) compounds [7, 11] were found for the first time.

[119]Sn Mössbauer results

Careful analysis of the magnetically split [119]Sn Mössbauer spectra allowed to monitor rare earth sublattice magnetisation as probed by diamagnetic tin ions. In general, the magnetic transition temperatures determined from the magnetic measurements and from Mössbauer spectroscopy show excellent agreement.

The Mössbauer spectra of REAuSn (RE = Gd-Er) compounds reveal a common pattern suggesting structural disordering effects: at low temperatures, magnetic hyperfine field distributions must be assumed to provide acceptable fits to the spectra [8–10, 12, 13]. On this basis, distribution phenomena can be a sign of possible crystallographic disorder of Au and Sn ions over the "In" sites within the CaIn$_2$-type of structure rather than ordered GaGeLi-type of structure [5]. Resonance spectra of REAuSn with light rare earths do not manifest magnetic disorder (as mentioned above) but another interesting behaviour can be observed, namely magnetic hyperfine field survives above critical temperature [3, 7, 11]. This can be explained in terms of spin correlations owing to short range order effects.

In accordance with the arguments given in Ref. [4], the direction of the V_{zz} axis of the EFG tensor in CaIn$_2$ (or GaGeLi) type of structure coincides with crystallographic c-axis. Furthermore, magnetic hyperfine field H_{hf} at tin site consists only transfer part H_{tr} (parallel to the magnetic moments) and dipolar contribution H_{dip}, which is small and usually negligible. Due to diamagnetic character of Au and Sn ions, total magnetic contributions come from rare earth neighbourhood. Owing to these facts, the θ angle which is defined as the angle between the direction of the V_{zz} axis of the EFG tensor and the direction of magnetic hyperfine field H_{hf}, is a good measure of the angle between the crystallographic c-axis and the direction of the rare earth magnetic moments determining the easy axis of magnetisation. As it can be seen in Fig. 2, the easy axis of magnetisation is close to the crystallographic c-axis in REAuSn compounds, except for CeAuSn. It should be pointed out that in the case of DyAuSn there was a strong suggestion that two sets of hyperfine parameters with different signs of splitting constants and θ angles
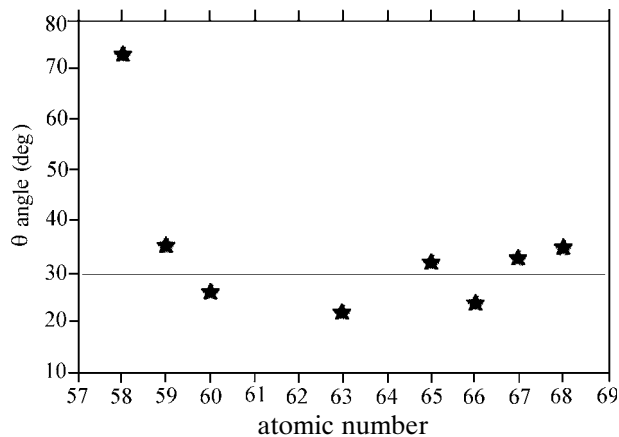

Fig. 2. θ angles derived from [119]Sn Mössbauer spectra obtained for hexagonal REAuSn compounds.
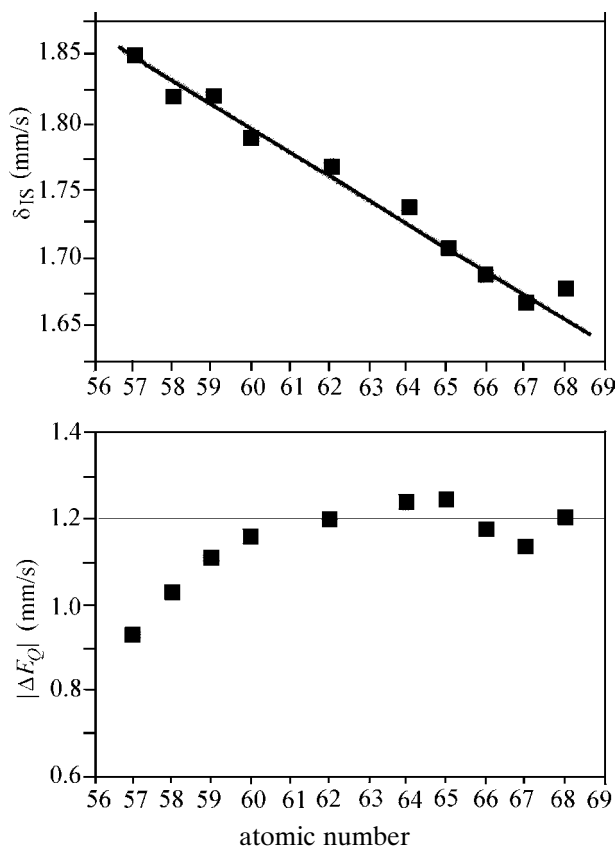
Fig. 3. Isomer shifts and absolute quadrupole interaction constants derived from ^{119}Sn Mössbauer spectra obtained for hexagonal REAuSn compounds.

($\theta = 90°$ and $33°$) are possible [12]. The set with negative quadrupole interaction constant, giving θ angle equal to $33(1)°$, was found to follow the experimental trend shown in Fig. 2.

The measured values of ^{119}Sn isomer shifts are in the typical range for tin atoms in equiatomic inter-metallic ternary stannides being indicative of the proximity of the electronic structure of tin to the divalent state. They follow the trend observed for the *a*-lattice parameter and their consecutive, almost linear, reduction reflects the known lanthanide contraction (see Fig. 3).

The change of absolute values of quadrupole interaction constants versus atomic number of RE element was also derived from the ^{119}Sn resonance spectra (see Fig. 3).

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