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STRUCTURE AND MAGNETIC PROPERTIES OF TERNARY R-GE-SN SYSTEMS

Abstract. The structure and magnetic properties of ternary R-Ge-Sn systems are discussed in this article. Results obtained for these compounds should help to determine the role of p-electron atoms in the magnetic ordering.

Keywords: intermetallic compounds, crystal structure, magnetic structure, neutron diffraction.

Introduction

A new family of ternary intermetallic compounds with rare-earth (R), germanium (Ge) and tin (Sn) appeared recently. The compounds with formulas $RSn_{1+x}Ge_{1-x}$ (x ≈0.1) where R=Gd-Tm [1, 2], $R_2[Sn_xGe_{1-x}]_5$ (x≈0.25–0.3) and $R[Sn_xGe_{1-x}]_2$ (x≈0.2–0.25) [3] crystallize with the centrosymmetric space group Cmcm (No. 63) and the structures of these families can be described as built of two groups of anions: Ge zig-zag chains and square sheets (or double square sheets) of Sn atoms, with rare-earth cations enclosed between them. This is the unusual example of site preferences between elements from the same group. The structure and properties of ternary R-Ge-Sn systems are discussed in details. Results obtained for these compounds should help to determine the role of p-electron atoms in the magnetic ordering.

Methods of investigation

Polycrystalline samples of $RSn_{1+x}Ge_{1-x}$ (R = Tb, Dy, Ho, Er, x ≈ 0.1), $TbSn_{0.4}Ge_{1.4}$ and $NdSn_{0.62}Ge_{1.775}$ were synthesized by arc melting high purity elements (R: 99.9 wt %; Sn and Ge: 99.99 wt. %) in a titanium-gettered argon atmosphere. Afterwards, the samples were annealed in evacuated quartz am-

poules at about 800 K for one weak. The stoichiometry of the samples was controlled by weight before and after the melting. The differences were smaller than 0.5%.
The samples were checked by X-ray powder diffraction at room temperature on a Philips PW-3710 X'PERT diffractometer using CuKα radiation. The magnetic measurements were carried out using a vibrating sample magnetometer (VSM) option of the Quantum Design PPMS platform.
The neutron diffraction patterns were collected at temperatures ranging from 1.45 to 37.6 K on the E6 diffractometer installed at the BER II reactor (BENSC, Helmholtz-Zentrum Berlin). The incident neutron wavelength was 2.447 Å.

Results

The X-ray analyses of the samples performed at room temperature indicated that the compounds have the orthorhombic crystal structure of $CeNiSi_2$-type [5] described by the space group Cmcm (No. 63). In this crystal structure, the atoms in the unit cell occupy four nonequivalent sites and form the layers stacked along the b-axis. In the concerned compounds the vacancies are detected. The influence of these vacancies on the magnetic ordering is the interesting problem for investigations.

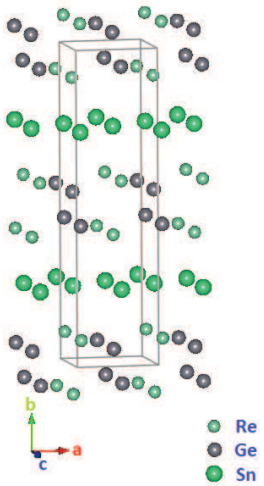

Fig. 1. Projection of the crystal structure of R-Sn-Ge

The $RSn_{1+x}Ge_{1-x}$ compounds are antiferromagnets at low temperatures [3]. The magnetic ordering in $TbSn_{1.12}Ge_{0.88}$ is sine-modulated described by the propagation vector k=(0.4257(2), 0, 0.5880(3)). Tb magnetic moment equals 9.0(1) μ_B at 1.62 K. It lies in the *b–c* plane and form an angle θ=17.4(2)° with

the *c*-axis. This structure is stable up to the Néel temperature equal to 31 K. The magnetic structures of $RSn_{1+x}Ge_{1-x}$, where R = Dy, Ho and Er at low temperatures are described by the propagation vector k=(1/2, 1/2, 0) with the sequence (+ + – +) of magnetic moments in the crystal unit cell. In $DySn_{1.09}Ge_{0.91}$ and $HoSn_{1.1}Ge_{0.9}$ magnetic moments equal 7.25(15)) μ_B and 8.60(6) μ_B at 1.55 K, respectively. The moments are parallel to the *c*-axis. For Ho-compound this ordering is stable up to T_N=10.7 K. For $ErSn_{1.08}Ge_{0.92}$, the Er magnetic moment equals 7.76(7) μ_B at T=1.5 K and it is parallel to the *b*-axis. At T_t=3.5 K it tunes into the modulated structure described by the k=(0.496(1), 0.446(4), 0). With the increase of temperature there is a slow decrease of k_x component and a quick decrease of k_y component. The Er magnetic moment is parallel to the *b*-axis up to 3.9 K while at 4 K and above it lies in the *b*–*c* plane and form an angle 48(3)° with the c-axis. In compounds with R=Tb, Ho and Er the magnetostriction effect at the Néel temperature is observed. The magnetic structures of $RSn_{1+x}Ge_{1-x}$ compounds are shown in Fig. 2.

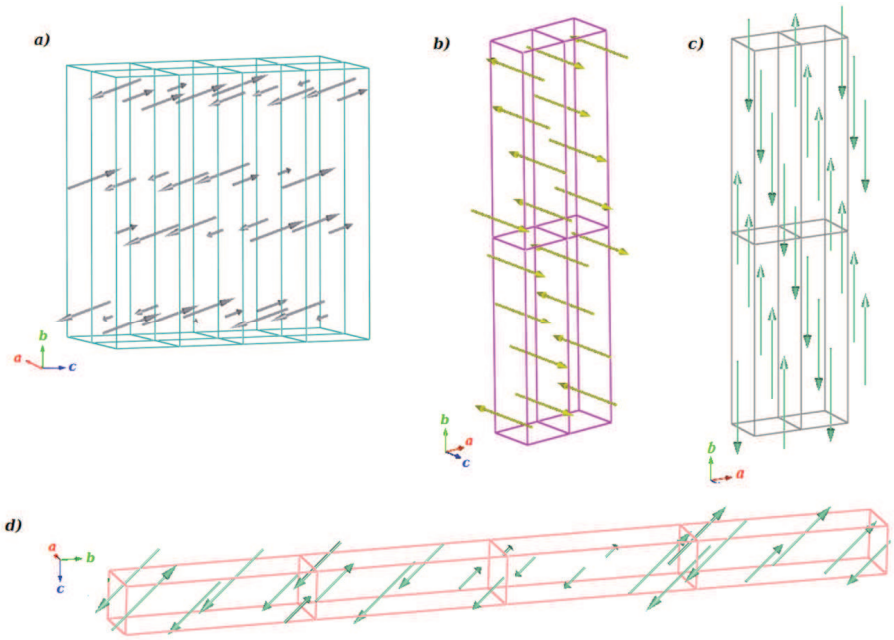

Fig. 2. The magnetic structures of $RSn_{1+x}Ge_{1-x}$ (R = Tb, Dy, Ho and Er, $x \approx 0.15$) compounds determined by neutron diffraction studies on polycrystalline samples [3]. The magnetic ordering in $TbSn_{1.12}Ge_{0.88}$ (a) is sine-modulated described by the propagation vector k = (0.426, 0, 0.588). The magnetic structures of $RSn_{1+x}Ge_{1-x}$ where R = Dy, Ho (b) and Er (c) at temperatures close to 1.5 K are described by the propagation vector k = (½, ½, 0) with the sequence (+ + – +) of magnetic moments in the crystal unit cell. For Ho- and Dy-compound this ordering is stable up to T_N while for Er-compound at T_t = 3.5 K it tunes into a modulated structure (d)

The values of the respective Neel temperatures for Tb-, Ho- and Er-compounds, determined by means of the neutron diffraction studies, are in good agreement with previously published ones based on the magnetic and specific heat data [1].

In the investigated $RSn_{1+x}Ge_{1-x}$ compounds the large R – R interatomic distances, about 4 Å in the *b–c* plane and 3.5 Å along the *b*-axis, and metallic character of the electrical resistivity [1] indicate that the magnetic ordering in the rare earth sublattice is realized by the magnetic interactions with the conduction electrons (RKKY interaction). The RKKY interactions are long-range and this should lead in general, to modulated magnetic structures. The determined magnetic structures have such character. The change of magnetic structure from the collinear commensurate to the modulated incommensurate observed in $ErSn_{1.08}Ge_{0.92}$ with increase of temperature is quite common among rare earth intermetallics and may be explained as a result of a competition between different types of interactions.

In the investigated $RSn_{1+x}Ge_{1-x}$ compounds for R=Tb, Dy and Ho the magnetic moments are smaller than for free R^{3+} ion values. This indicates the influence of the crystal electric field. The orientation of the rare-earth magnetic moments also confirms the influence of the CEF effect.

The temperature dependences of the magnetic susceptibility measured in the magnetic field of 50 Oe and magnetization curves of $TbSn_{0.4}Ge_{1.4}$ and $NdSn_{0.62}Ge_{1.775}$ compounds are shown on Fig. 3 and are described in Ref. 4. The measurements gave the maximum at 22 K and an additional small anomaly at 13.2 K for Tb-compound and the two maxima at 3.7 and 5.1 K for Nd-compound. The differences between ZFC and FC curves above the Neel temperatures were also observed. This may suggest that above the Néel temperature the short range ordering exists. With decrease of temperature at T_N the long-range antiferromagnetic ordering is stable. The magnetic moment at low temperatures are much smaller than the free R^{3+} ion values. The additional anomaly observed for $TbSn_{0.4}Ge_{1.4}$ and $NdSn_{0.6}Ge_{1.775}$ below T_N is probably connected with the change of the magnetic properties.

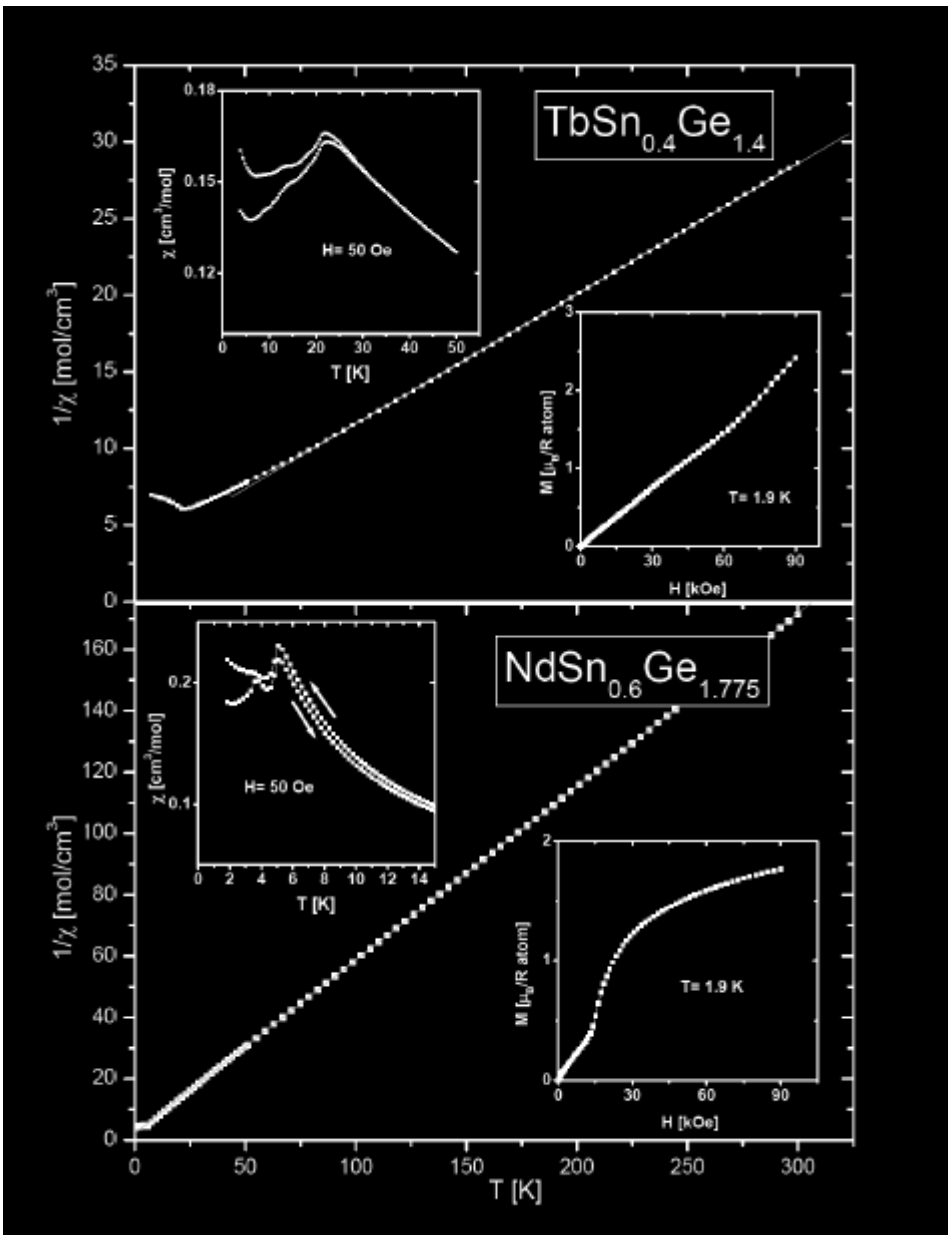

Fig. 3. Temperature dependence of the reciprocal magnetic susceptibility measured at 1kOe magnetic field for $TbSn_{0.4}Ge_{1.4}$ and $NdSn_{0.6}Ge_{1.775}$. Insets shows: temperature dependence of the magnetic susceptibilities (ZFC – lower curve and FC – upper curve) and the magnetization curve up to 90 kOe at T=1.9 K [4]

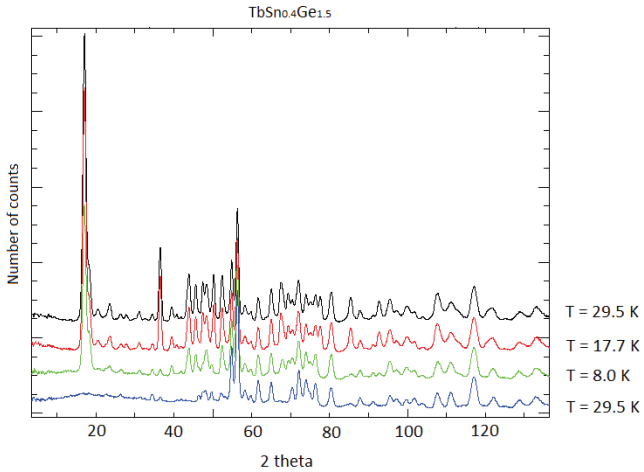

Fig. 4. Neutron diffraction patterns of $TbSn_{0,4}Ge_{1,5}$

The neutron diffraction measurements were performed for the sample of $TbSn_{0.47}Ge_{1.47}$ in four temperatures: 2.7, 8.0, 17.7 and 29.5 K in the angles range of 3.5–137 degrees (Fig. 4). In addition, the temperature dependencies were measured in 21 different temperatures to determine the Neel temperature and to see what happens with the magnetic structure. The measurements have shown that this compound become antiferromagnetic below 25.5 K. Additionally the change in the magnetic ordering is observed below 17.7 K (Fig. 5).

More detailed analysis will be carried out.

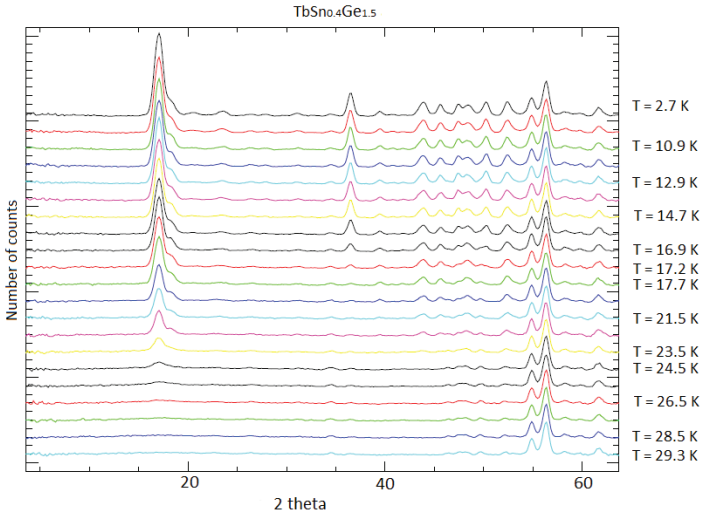

Fig. 5. Part of the neutron diffraction patterns of the $TbSn_{0.4}Ge_{1.5}$ measured at different temperatures between 2.7 and 29.3 K

The neutron diffraction pattern of the sample $Nd_2Sn_{1.24}Ge_{3.55}$ was different than measured in X-ray diffraction measurement, in the meantime it changed its colour – the most probably, the sample has been destroyed.

Summary

The analysis of the magnetic properties in R-Sn-Ge systems shows similarities to the RT_xX_2 compounds [6]. The Nèel temperatures for both series of compounds are also similar. The neutron diffraction data indicates that the magnetic moment is localized on the rare-earth atoms. The large R–R interatomic distances and metallic character of the electrical resistivity suggest that interaction between magnetic moments takes place via conduction electrons. Another factor which affects the magnetic ordering in these compounds is the crystal electric field (CEF) effect which determines the direction of a magnetic moment.
After comparison of the magnetic properties for both groups of compounds it can be inferred that other elements (T, Sn, Ge) have not got significant influence on stability of the magnetic ordering.

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STRUKTURA I WŁASNOŚCI MAGNETYCZNE TRÓJSKŁADNIKOWYCH ZWIĄZKÓW R-GE-SN

Streszczenie

W artykule omówiono szczegółowo budowę i właściwości magnetyczne trójskładnikowych układów R-Ge-Sn. Wyniki uzyskane dla tych związków powinny pomóc określić rolę atomów p-elektronowych w oddziaływaniu magnetycznym.

Słowa kluczowe: związki międzymetaliczne, struktura krystaliczna, struktura magnetyczna, dyfrakcja neutronów.