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Structural studies of liquid Co–Sn alloys

A. Yakymovych^{a,*}, I. Shtablayvi^b, S. Mudry^b^a Department of Inorganic Chemistry (Materials Chemistry), University of Vienna, Währinger Str. 42, 1090 Vienna, Austria^b Department of Metal Physics, Ivan Franko National University, Kyrylo i Mephodiy Str. 8, 79005 Lviv, Ukraine

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ABSTRACT

An analysis of the structure features of liquid Co–Sn alloys has been performed by means of X-ray diffraction method, viscosity coefficient analysis and computer simulation method. The X-ray diffraction investigations were carried out over a wide concentration range at the temperature 1473 K. It was found that the structure of these alloys can be described in the frame of independent X-ray scattering model. The viscosity coefficient was calculated by an excess entropy scaling and compared with experimental data.

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1. Introduction

The phase diagram of Co–Sn system has changed significantly in the last decade mainly because of the finding out of previously unknown CoSn₃ compound [1–5]. Meanwhile according to the different works the melting temperatures for key compositions have dissimilar values such as Co₃Sn₂ compound (~1473 K [1], ~1443 K [2,3], and ~1453 K [4,5]) as well as an eutectic point (~1398 K [1], ~1385 K [2,3], ~1323 K [4], and ~1376 K [5]). Moreover the composition of the eutectic point is also under discussion [6]. The mentioned above discrepancies in the data could be connected with experimental difficulties due to a high diffusion of the cobalt in tin [7], meanwhile in [8] is mentioned the very small diffusion mobility of the Co atoms in the Co-based alloys.

An industrial point of view the investigations of Co–Sn alloys are motivated with possibility of using as a high-tech materials. As an example, such alloys might be appropriate for the production of Co–Sn-based metallic glasses [9] as well as for anode materials in lithium ion batteries [10].

There are several works dedicated to the investigations of the structure of Co–Sn alloys in the liquid state [11–16]. Based on the obtained results authors suggest the complex structure of the liquid Co–Sn alloys, but with the existence of different structure units. It should be noted that several Co-based systems reveal significant structure transformations with the concentration and composition changes in the liquid state [15]. Such structure anomalies bring to deviations of the structure sensitive properties from

the ideal behavior: the concentration dependence of the activation energy of viscous flow of liquid Co–Sn alloys is similar to the liquidus curve of the phase diagram and shows an unexpected increase near the eutectic concentration [17]; the surface tension data versus concentration have a negative deviation from the Raul's law at 1823 K [18]. Besides, the enthalpy of mixing shows the temperature dependence with more negative values at lower temperatures [19]. On the other hand, there is some disagreement in the analysis of the experimental data. For example, the author of [20] supposed the existence of associates with the stoichiometry of Co₂Sn-type, while in Ref. [13] postulated a formation of Co₃Sn₂-type associates has a main impact on the structure of liquid Co–Sn alloys. According to [15], in melts are present the atomic coordinations with markedly different interatomic distances. The purpose of this work is to clarify information on the structure of liquid Co–Sn alloys available in literature. The main point of the presented study as continuation of the our previous works [11–14] is the investigations of the liquid Co–Sn alloys over the wide concentration range at the temperature 1473 K, which is close to the melting point of component with the highest melting temperature. In this case a presence of structural units with intermetallic like chemical short range order in the melts is expected. Thereby, based on the experimental results and model simulations the composition changes of structure units with concentration were studied. Other words, the detected structure features with change of the concentration of liquid Co–Sn alloys were more in the detail analyzed in comparison with early published works [11–14] more dedicated on the temperature dependence of the structure characteristics.

The obtained data on structure were used for calculation of the concentration dependence of viscosity coefficient, which is one of

* Corresponding author. Tel.: +43 69919097978.

E-mail address: andriy.yakymovych@univie.ac.at (A. Yakymovych).

the main structure-sensitive properties of the liquid state. A semi-empirical universal relationship proposed by Rosenfeld [21] and a universal scaling law proposed by Dzугutov [22] are used for the concentration dependence of the viscosity calculations. The modeled viscosity values are compared with literature data.

2. Experimental and RMC modeling

Ingots of tin and cobalt (both of 99.99% purity) were used to prepare the alloy samples in an arc melting furnace.

The XRD measurements were carried out by means of a high-temperature X-ray diffractometer with a special attachment, which allows investigating the solid and liquid samples at different temperatures. Cu K α radiation monochromatized with LiF single crystal and Bragg–Brentano focusing geometry in the 2θ range from 10° up to 120° were used. Intensity curves were corrected on polarization and incoherent scattering [23]. After this procedure they were normalized to electron units by Krogh–Moe method [24]. A detailed description of the experimental technique was reported [25]. The measuring of scattered intensity was done with accuracy better than 2%. Main structure parameters obtained from structure factor (SF) and pair correlation function (PCF) were calculated according to Ref. [26]. Main structure parameters obtained from them were analyzed.

Details describing the RMC technique can be found in [27]. The initial cubic cell was arranged with 5000 atoms in the stoichiometric ratio, which corresponded to the melt composition. The sizes of the model cube were adapted with the melt density at the experiment temperature. The minimum distances between atoms r_{ij} was took the point of intersection of the left branch of the first maximum in an experimental PCF curve with the abscissa axis. According to the RMC algorithm, the model is optimized by minimizing the sum of the squared difference between experimental and model total structure factors according to equation:

$$\chi^2 = \sum_{i=1}^N (S^{sim}(k_i) - S^{exp}(k_i)) / \sigma^2(k_i), \quad (1)$$

where k_i is the wave vector; $\sigma^2(k_i)$ is the experimental error as a function of wave vector k ; S^{sim} and S^{exp} are the model and experimental total structure factors.

As a result of simulation the partial pair correlation function and Faber–Ziman partial structure factors have been obtained. Partial coordination numbers have been calculated by means of analysis of local structure of the RMC simulated configurations.

3. Results and discussion

Experimental SFs for liquid $\text{Co}_{100-x}\text{Sn}_x$ alloys of different Co content show the untypical for simple liquids profile (Fig. 1). Particularly the principal peak is low, wide and reveals a fine structure comparatively to SFs of constituents. Because of the existence of several intermetallic compounds the local atomic structure in the Co–Sn alloys should be significantly depend from the concentration of components both in the solid and in the liquid state that is evidently observed in SFs at different content of the components. The splitting of broad main SF maximum of liquid Co–Sn alloys into two sub-peaks at some concentrations is one of the confirmations of a complex structure of the investigated alloys. The first sub-peak corresponds to the main SF maximum of liquid Sn, while the second one corresponds to the position of the main SF maximum for liquid Co (Fig. 1). In this case the short range order structure in the liquid Co–Sn alloys cannot be described by a random atomic distribution and most probably could be interpreted as mixture of different kind structural units in the liquid state.

In view of the formation of chemical compounds in the investigated system and taking into account an exothermic behavior of the integral enthalpy of mixing with minimum point of about 60 at.% Co [19] we can assume the existence of complexes (clusters) with similar chemical ordering in the liquid state. It should be also noted, that among all existing compounds, and only Co_3Sn_2 melts uniformly reaching a congruent melting point and is most stable compound in the system. As follows from structural studies for such kind compounds the chemical ordering persists upon melting. Therefore we can suppose that this compound will affect the structure of the Co–Sn alloys in the liquid state. Accordingly, the composition which corresponds to the Co_3Sn_2 compound

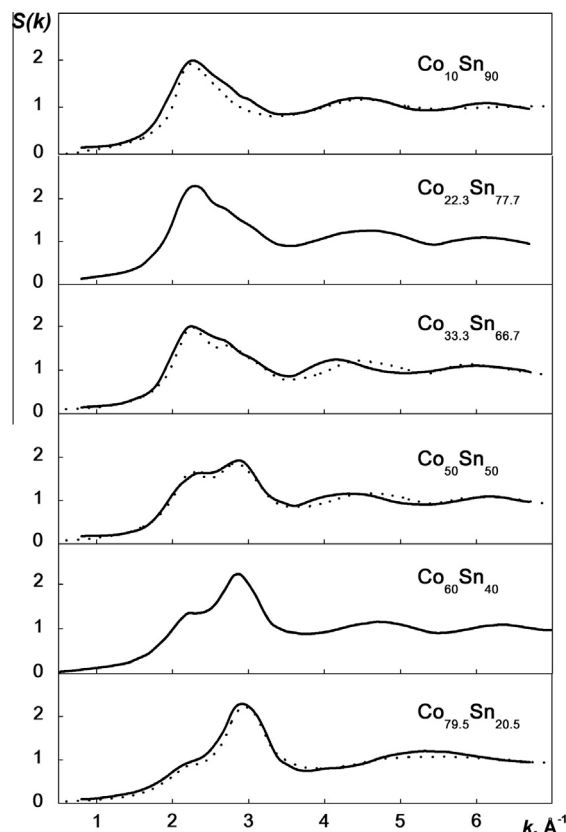


Fig. 1. Structure factors for liquid Co–Sn alloys.

divides the phase diagram into two parts. The first part is a eutectic type diagram, and the second one – eutectic type with incongruent melting phases. Thus, we will consider the structure of the investigated liquid alloys in accordance with above mentioned feature of phase diagram.

Liquid $\text{Co}_{79.5}\text{Sn}_{20.5}$ alloy corresponds to the eutectic composition which consists from pure cobalt and Co_3Sn_2 phase in the solid state. According to the self-associated model the liquid eutectics consist of clusters with structure corresponding to the phases formed according to eutectic reaction $L \rightarrow \text{Co} + \text{Co}_3\text{Sn}_2$. According to Ref. [16] $\beta\text{Co}_3\text{Sn}_2$ - and βCo -type clusters exist in the liquid $\text{Co}_{79.5}\text{Sn}_{20.5}$ alloy in the temperature range 1423–1623 K. Therefore we have compared the structure factors of the liquid $\text{Co}_{50}\text{Sn}_{50}$, $\text{Co}_{60}\text{Sn}_{40}$ and $\text{Co}_{79.5}\text{Sn}_{20.5}$ alloys with the diffraction pattern of the crystalline Co_3Sn_2 (Fig. 2). As we can see from the figure, comparison shows a good agreement. This also allowed us to suppose that Co_3Sn_2 -like chemical ordered units affects the structure over the whole investigated concentration range.

For more detailed investigation of the structure, we performed modeling the structure of investigated alloys by reverse Monte Carlo method. As a result of simulation, partial structure factors (PSF) and pair correlation functions (PPCF) were obtained. Using the partial pair correlation functions partial interatomic distances were defined.

Fig. 3 shows partial SFs of liquid Co–Sn alloys compared with diffraction pattern for the crystalline Co_3Sn_2 . As can be seen, if the content of tin in melts is less than 50%, the positions of the main maxima of the partial structure factors $S_{\text{Co-Sn}}(k)$ coincide with reflexes of crystalline compound indicating the existence clusters with Co_3Sn_2 -type chemical short-range order in the melt. With increasing of tin content, the effect of chemically ordered atomic groups on the structure of alloys becomes smaller. Preferred interaction of different kinds of atoms confirms the

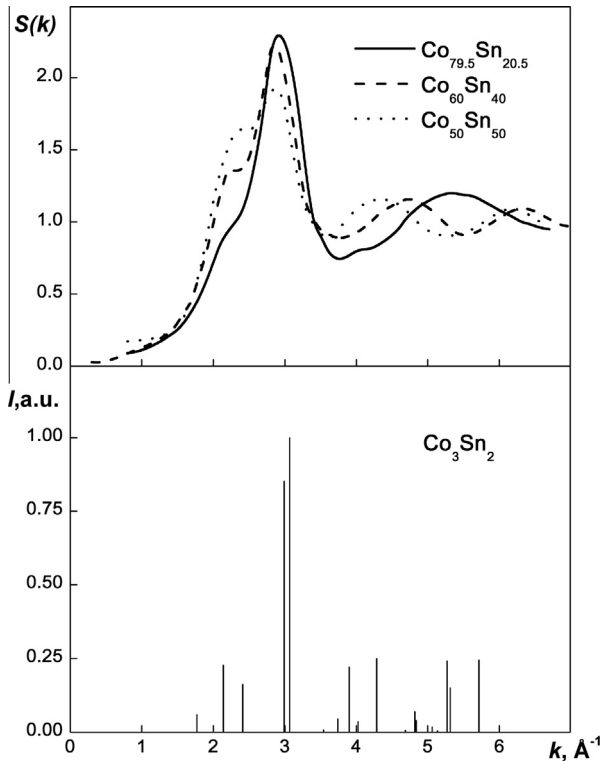


Fig. 2. Structure factors for liquid $\text{Co}_{50}\text{Sn}_{50}$, $\text{Co}_{60}\text{Sn}_{40}$ and $\text{Co}_{79.5}\text{Sn}_{20.5}$ alloys and diffraction pattern for crystalline Co_3Sn_2 compound.

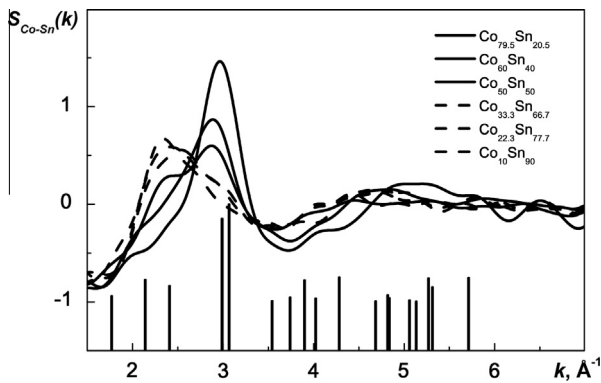


Fig. 3. Partial structure factors for liquid Co-Sn alloys and diffraction pattern for crystalline Co_3Sn_2 compound.

reduction of average interatomic distances $r_{\text{Co-Sn}}$ in comparison with the sum of Sn and Co radii (Fig. 4). Weightier evidence of the existence of Co_3Sn_2 -type chemical short-range order is the comparison the partial interatomic distances and coordination numbers of investigated liquid alloys and crystalline compound. According to [28] for crystalline Co_3Sn_2 phase, tin has 6 Sn atoms as a nearest neighbors at a distance of 3.52 Å, 5 Co atoms as neighbors (3 + 2 at a distance of 2.36 Å and 2.61 Å respectively) whereas cobalt has 8 neighbors of Co (2 + 6 at a distance of 2.61 Å and 2.70 Å respectively). As we can see from Figs. 4 and 5 the partial interatomic distances and coordination numbers are in good agreement with the above data.

To confirm hypothesis about formation of Co_3Sn_2 -type chemical ordering groups (clusters) in Co-Sn melts the structure factors of melts in the frame of independent scattering model have been calculated. According to this model, the intensity of X-ray scattering by alloy is equal to the weighted sum of scattered intensities of the alloy components

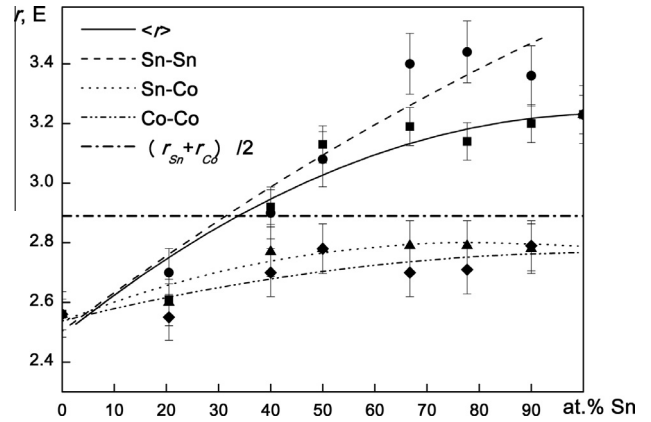


Fig. 4. Concentration dependence of interatomic distances for Co-Sn liquid alloys.

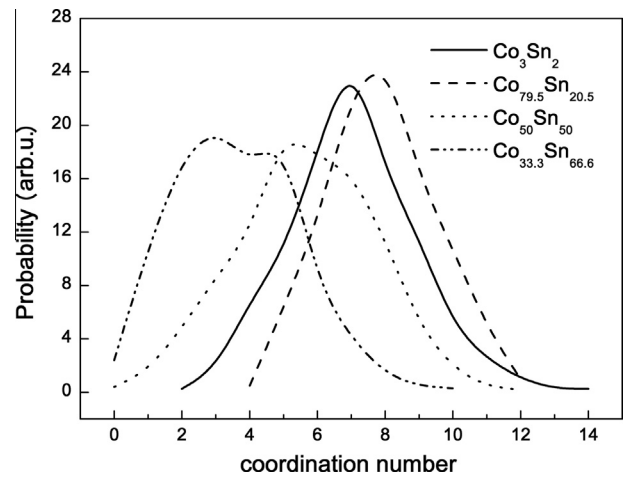


Fig. 5. Probability of the Sn-Co partial coordination numbers in the liquid state.

$$I_a = c_1 I_1 + c_2 I_2, \quad (2)$$

where I_a , I_1 , and I_2 are the intensities of X-ray scattering; c_1 , c_2 are the fractions of the alloy components. Using this relation we can calculate the structure factor of the alloy:

$$S(k) = c_1 K_1^2 S_1(k) + c_2 K_2^2 S_2(k), \quad (3)$$

where $K_1^2 = \frac{F_1^2(k)}{c_1 F_1^2(k) + c_2 F_2^2(k)}$, $K_2^2 = \frac{F_2^2(k)}{c_1 F_1^2(k) + c_2 F_2^2(k)}$ are the scattering abilities of the alloy components; F_1 , F_2 are the atomic scattering factors.

The calculation results are shown in Fig. 1 (dot line). Calculations were carried out assuming that the structure of melts containing less than 40 at.% of tin forms with clusters of cobalt and Co_3Sn_2 -type chemical ordering regions. The structure of alloys with higher content of tin affect chemically ordered Co_3Sn_2 clusters, solution with the composition $\text{Co}_{22.3}\text{Sn}_{77.7}$ for liquid $\text{Co}_{50}\text{Sn}_{50}$ or $\text{Co}_{33.3}\text{Sn}_{66.7}$ and Sn for liquid $\text{Co}_{10}\text{Sn}_{90}$ alloys. According to Fig. 1 calculated curves are in good agreement with the experimental data. It should be noted that calculated curve for eutectic alloy is in good agreement with the experimental structure factor supposing the higher solubility of Co in the Co_3Sn_2 -type structural units comparatively with crystalline intermetallic. This solubility reaches values of about 70 at.% that is close to the Co_2Sn composition. This assumption follows from the fact that the stoichiometric range of Co_3Sn_2 -compound expands and shifts to the cobalt side of phase diagram at approaching to melting point. Calculation of other structure factors was based on the assumption that the composition of Co_3Sn_2 -like clusters corresponds to $\text{Co}_{60}\text{Sn}_{40}$

stoichiometry. Taking into account a good agreement of the experimental SFs with the calculated ones, we suppose that the structure of liquid alloys in the wide investigated concentration range can be represented as a mixture of two types of clusters, composition and relative content of which are given in Table 1. The standard deviation of represented data of cluster composition of Co–Sn liquid alloys in the frame of independent scattering model is less than $\pm 3\%$.

Combining the X-ray diffraction data and an excess entropy scaling, the concentration dependence of the viscosity for liquid Co–Sn alloys at 1473 K was calculated. By performed calculations of the viscosity we supposed that obtained by Fourier transformation of the SF values of the configuration entropy correspond to the excess entropy data.

The Rosenfeld's scaling law has been used for the calculations of the viscosity [21]:

$$\eta = \eta_R^* \rho^{2/3} (mk_B T)^{1/2}, \quad (4)$$

where ρ is the density; m is the atomic mass; k_B is the Boltzmann constant; T is the temperature; and the reduced viscosity coefficient according to the Rosenfeld:

$$\eta_R^* = 0.2e^{-0.8S}, \quad (5)$$

where S is the excess entropy.

In another way, microscopic reduction parameters (collision frequency Γ and interparticle distance σ) were chosen for the transport coefficients, according to the Enskog theory [29]:

$$\Gamma = 4\sigma^2 g(\sigma) \rho \left(\frac{\pi k_B T}{m} \right)^{1/2}, \quad (6)$$

where $g(\sigma)$ is the radial distribution function at the position of the first maximum of the $g(r)$.

Using the microscopic reduction parameters Dzугutov [22] defined the follow relationship between the viscosity coefficient and reduced viscosity coefficient:

$$\eta = \eta_D^* \left(\frac{\Gamma m}{\sigma} \right), \quad (7)$$

where the reduced viscosity coefficient is equal:

$$\eta_D^* = 0.035e^{-0.55S}. \quad (8)$$

The density values were calculated for the melts from the densities of the constituents, ρ_i under the assumption that the excess volume is zero [30].

The comparison of the calculated viscosity of liquid Co–Sn alloys with literature ones [17] is shown in Fig. 6. The calculated viscosity data are in good agreement with experimental ones for the liquid $\text{Co}_{79.5}\text{Sn}_{20.5}$, $\text{Co}_{60}\text{Sn}_{40}$ and $\text{Co}_{50}\text{Sn}_{50}$ alloys, but are in disagreement for liquid $\text{Co}_{33.3}\text{Sn}_{66.7}$, $\text{Co}_{22.3}\text{Sn}_{77.7}$ and $\text{Co}_{10}\text{Sn}_{90}$ alloys, except calculated value using Eq. (7) for eutectic alloy. It means that by the predictions of η for liquid Co–Sn alloys with large amounts of tin should be consider various factors that account the specific atomic and electronic structure of liquid tin, which is commonly referred to semimetals. The compared analysis of

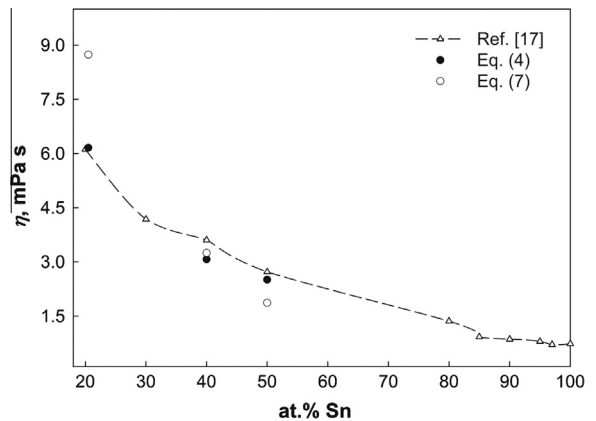


Fig. 6. Concentration dependence of the viscosity for liquid Co–Sn alloys at 1473 K.

experimental viscosity data with calculated ones using different semi-empirical models has been done in Ref. [17]. The main reason of performed calculations is to show the impact of the structure features on the viscosity, as one of the structure-sensitive properties. The agreement between experimental and calculated viscosity values for the liquid Co-based Co–Sn alloys suggests that the Co_3Sn_2 -like clusters formations should have a main impact on the structure-sensitive properties, while by calculations for the Sn-based alloys other factors should be also taken into account.

4. Conclusions

The asymmetry of the main peak of structure factors for liquid Co–Sn alloys indicates the existence of inhomogeneous short range order structure. The atomic arrangement of these alloys over the whole investigated concentration range can be described in the frame of independent scattering model. According to this model, the structure of melts containing less than 40 at.% of tin forms with clusters of cobalt and Co_3Sn_2 -type chemical ordering regions. The structure of alloys with higher content of tin affect chemically ordered Co_3Sn_2 clusters, solution with the composition $\text{Co}_{22.3}\text{Sn}_{77.7}$ for $\text{Co}_{50}\text{Sn}_{50}$ or $\text{Co}_{33.3}\text{Sn}_{66.7}$ melts and Sn for $\text{Co}_{10}\text{Sn}_{90}$ liquid alloy. The agreement between experimental and calculated viscosity values for the liquid Co-based Co–Sn alloys suggests that the Co_3Sn_2 -like clusters formations have a main impact on this transport property. Some discrepancy appears at increasing of Sn content in alloy due to the specific atomic and electronic structure of liquid tin.

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Table 1

Cluster composition of Co–Sn liquid alloys in the frame of independent scattering model.

Alloys	Clusters			
	Co	Co_3Sn_2	$\text{Co}_{22.3}\text{Sn}_{77.7}$	Sn
$\text{Co}_{79.5}\text{Sn}_{20.5}$	0.6	0.4	–	–
$\text{Co}_{50}\text{Sn}_{50}$	–	0.74	0.26	–
$\text{Co}_{33.3}\text{Sn}_{66.7}$	–	0.7	0.3	–
$\text{Co}_{10}\text{Sn}_{90}$	–	–	0.04	0.96

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