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Peculiarities of Crystal Structure and Superfine Interactions in Alloys Ti-Co-Sn

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Alloys with general formula $\text{TiCo}_{2-x}\text{Sn}$ ($0 \leq x \leq 1.0$) were produced by way of sintering primary components – pure metals in an argon atmosphere. The alloys were homogenized by annealing in the evacuated quartz vessel at $T = 1070$ K during 500 h. X-ray diffraction analysis confirmed single-phased condition of all samples.

Nuclear gamma resonance (NGR) analysis was made at $T = 295$ and 80 K using radiation source $\text{BaSn}^{119}\text{Sn}$. It was established, that Sn atoms in samples with $x = 0.6$ and 1.0 are in two crystallographic positions, pyramids (1) and tetrahedrons (2) to which isomer shifts correspond (relative to SnO_2 1.52 - 1.65 mm/s for Sn(1) and 2.99 mm/s for Sn(2). Zeeman splitting for Sn(1) in TiCo_2Sn takes place at $T = 295$ and 80 K, and for compositions with $x = 0.3 - 1.0$ at $T = 80$ K only. For Sn(2) it is noted only in alloy TiCoSn at $T = 80$ K. The conclusion has been made on the reason of formation of effective magnetic fields on non-magnetic tin atoms nuclei.

Keywords: Heusler phases, nuclear gamma resonance, magnetic field, isomeric shift.

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Introduction

There are known works, for example [1], where the alloys MeCo_2Sn ($\text{Me} = \text{Ti}, \text{Zr}, \text{Hf}$) have been studied using NGR method. Such alloys are attributed to Heusler phases whose magnetic and electric properties depend not only on the chemical nature of the element Me, but also on the degree of their lattice perfection [2, 3]. As of today there is still no clear understanding of the mechanism of formation of magnetic superfine interactions for the non-magnetic Sn atom in MeCo_2Sn phases. This is why investigation of magnetic fields on tin atoms nuclei in isostructural alloys with MeCo_2Sn phase is important for resolving this problem.

This paper deals with the establishment of interrelation of the strength of magnetic field on tin atoms in solid solutions $\text{TiCo}_{2-x}\text{Sn}$ and their composition and peculiarities of crystal structure.

It is known, that alloys $\text{TiCo}_{2-x}\text{Sn}$ form solid solutions whose homogeneity includes values $x = 0.0 \dots 1.0$ [4]. The alloy in this series - TiCo_2Sn ($x = 0.0$) is attributed to space group $\text{Fm}\bar{3}\text{m}$ [5]. Unit cell of TiCo_2Sn it is shown in Fig. 1. Tin atoms in the structure of this alloy, we shall indicate them as Sn(1), form a dense cubic packing where tetrahedral and octahedral positions are filled by Co and Ti atoms respectively. The eight Co atoms are located in the first coordination sphere of Sn(1) atoms, in the second – six Ti atoms. X-ray diffraction analysis has shown, that TiCoSn alloy has a crystal structure that is a defective derivative of TiCo_2Sn alloy structure where Co atoms occupy only half of tetrahedral positions [6, 7].

The other half of positions that are not filled by Co atoms forms tetrahedral vacancies in TiCoSn crystal lattice. However, as the results of precision X-ray diffraction analysis and the structure calculations, an excess over stoichiometric composition of Co and tin

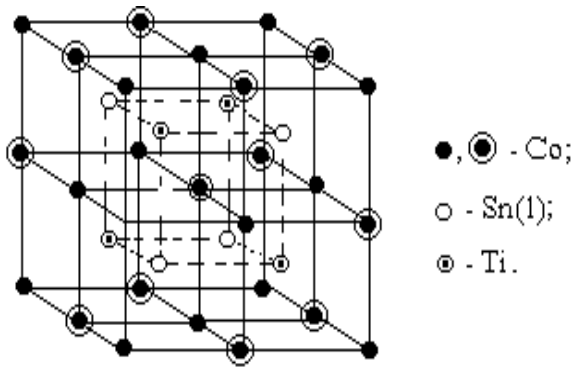


Fig. 1. Unit cell of TiCo_2Sn alloy.

(Sn(2)) atoms, each by 0.14 at. parts that are statistically distributed in the formed tetrahedral vacancies [3], indicated in Fig. 1 by large circles. This is why in TiCoSn alloy in the immediate surrounding of Sn(1) atom there are four Co atoms, located in the vertices of the tetragonal pyramid, and Co and Sn(2) atoms, statistically distributed in tetrahedral vacancies. At the same time, Sn(2) atoms have a cubic surrounding of four Ti atoms and four Sn(1) atoms.

I. Preparation of samples, methods of investigations

Samples of $\text{TiCo}_{2-x}\text{Sn}$ alloys ($x = 0.0; 0.3; 0.6; 1.0$) were produced by arc-melting of pure metals containing at least 99.99 % of primary component in the atmosphere of purified argon. The alloys were homogenized by annealing in quartz vacuum vessels at $T = 1070$ K during 500 hours. X-ray diffraction analysis has shown that all prepared samples were single-phased.

NGR spectra by spectrometer with uniform acceleration were measured. $\text{BaSn}^{119}\text{O}_3$ was used as the gamma-ray source at room temperature. The absorption spectra were obtained at temperatures $T = 295$ K and 80 K on the samples that had natural concentration Sn^{119} . Absorber thickness attained 0.1 mg/cm^2 for Sn^{119} .

II. Results

Fig. 2 and 3 show NGR-spectra of $\text{TiCo}_{2-x}\text{Sn}$ alloys ($x = 0.0; 0.3; 0.6; 1.0$), and Table 1 shows results of calculations of their parameters. As follows from Fig. 2a, phase TiCo_2Sn absorption spectrum at temperature $T = 295$ K is characterized by a Zeeman structure. In the central part of the spectrum there is observed an overlapping of two separate resonance lines A_1 and A_2 with isomer shifts $\delta_1 = 1.14 \pm 0.02 \text{ mm/s}$ and $\delta_2 = 2.57 \pm 0.02 \text{ mm/s}$. As the calculations have shown, their intensities are practically the same and each attains of 7...8% of total spectrum area.

Paramagnetic components in Fig. 2a result from the presence in the sample of tin atoms that did not enter TiCo_2Sn phase. Measurement of NGR-spectra of TiCo_2Sn at $T = 295$ K in external field with induction

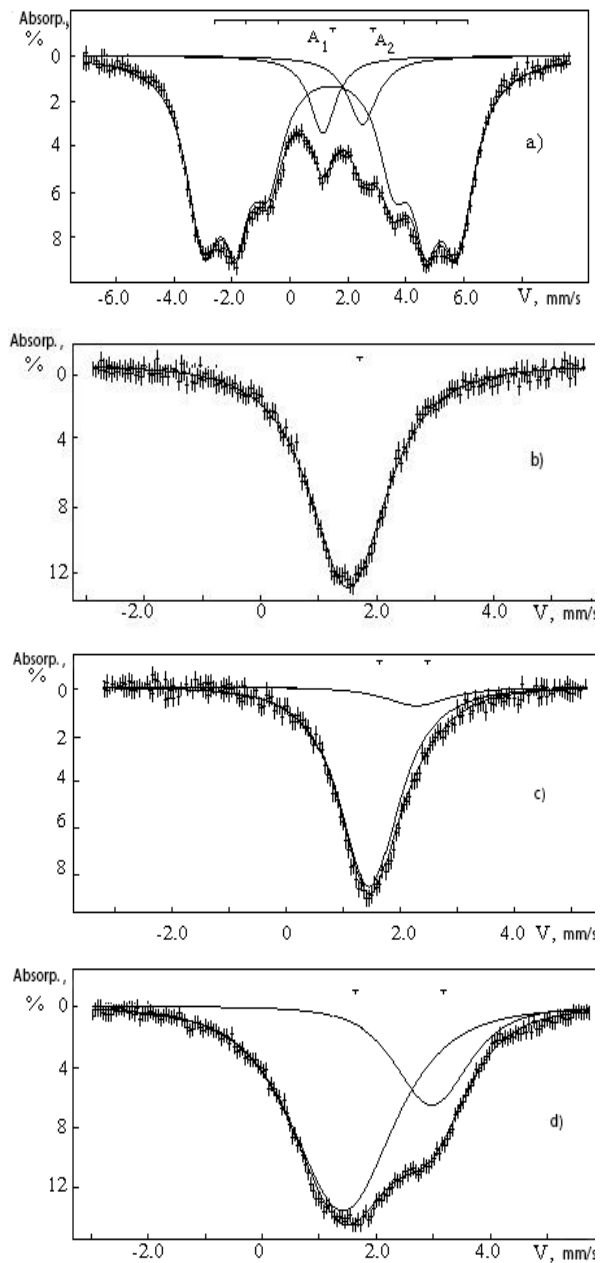


Fig. 2. NGR-spectra of $\text{TiCo}_{2-x}\text{Sn}$ alloys at $T = 295$ K: a) TiCo_2Sn ; b) $\text{TiCo}_{1.7}\text{Sn}$; c) $\text{TiCo}_{1.4}\text{Sn}$; d) TiCoSn .

$B = 1.6$ T has shown that the sign of the effective magnetic field H_{eff} on Sn(1) nuclei is positive, that is, its orientation coincides with orientation of Co atomic magnetic moments.

III. Discussion of results

In crystal structure of $\text{TiCo}_{1.7}\text{Sn}$ phase in comparison with TiCo_2Sn there are absent about 15 % of Co atoms which leads to the appearance of tetrahedral vacancies in $\text{TiCo}_{1.7}\text{Sn}$. NGR-spectrum of $\text{TiCo}_{1.7}\text{Sn}$ alloy at $T = 295$ K has the look of a broadened ($G_{1/2} = 1.54 \pm 0.02 \text{ mm/s}$) single line (Fig. 2b). Broadening of the resonance line is, probably, connected with statistical distribution of the formed vacancies relative to Sn(1) atoms. At transition of alloy $\text{TiCo}_{1.7}\text{Sn}$

to $\text{TiCo}_{1.4}\text{Sn}$ the resonance spectrum of the latter (Fig. 2c) shows an additional line with a greater value of isomer shift (Table 1), that corresponds to tin atoms Sn(2).

Let us turn our attention to the analysis of TiCoSn alloy absorption spectrum (Fig. 2d), in whose crystal structure there is absent already one half cobalt atoms. As it was mentioned above, Sn(1) atoms in this structure are located in the centers of pyramids formed by four atoms of cobalt, while the excessive atoms of tin Sn(2) and cobalt are located statistically in tetrahedral vacancies. In the result of overlapping of the lines of resonance absorption of gamma quanta by nuclei of Sn(1) and Sn(2) atoms a NGR-spectrum decomposed into two single lines was produced with the widths $G_{1/2} = 1.50 \pm 0.02$ mm/s characterized by different values of intensities and isomer shifts (Table 1). The greater value of isomer shifts for Sn(2) atoms compared to Sn(1) atoms testifies to the greater s-electron charges on Sn(2) nuclei which can be caused by the growth of chemical bonds covalence degree. As follows from our calculations, the number of Sn(1) atoms in TiCoSn is by 2.85 times greater than that of Sn(2) atoms.

As shown in [3], Curie temperature of alloys with $x = 0.0; 0.3; 0.6; 1.0$ attains 372, 218, 160 and 135 K respectively. The Zeeman picture of NGR-spectra of Sn^{119} in TiCo_2Sn is observed also at $T = 80$ K, and that for compounds with $x = 0.3; 0.6$ and 1.0 at $T = 80$ K is shown in Fig. 3, which indicates presence of the effective magnetic fields on tin atoms and magnetic ordering of the alloys. It has been established, that at transition from compound with $x = 0.0$ to $x = 1.0$ mean values of the effective magnetic fields H_{eff} on Sn(1) nuclei change non-monotonically (Fig. 4). There is observed an increase of H_{ef} values on sample with $x = 0.6$ in which are less magnetic Co atoms than in sample with $x = 0.3$. Such increase of H_{eff} is congruent with the highest value on the effective magnetic field on Co atoms in the series of alloys $0.3 \leq x \leq 1.0$ [3].

In test samples of $\text{TiCo}_{2-x}\text{Sn}$ alloys only cobalt atoms have a magnetic moment. Considering, that the distances between cobalt atoms in $\text{TiCo}_{2-x}\text{Sn}$ (3.00 \AA) exceed distances Co-Co in metal cobalt (2.51 \AA), magnetic ordering in $\text{TiCo}_{2-x}\text{Sn}$ alloys is evidently caused by indirect exchange interactions that have a long-range character. Such interactions may occur through polarization of conduction electrons and lead to

emergence of the effective magnetic fields on tin non-magnetic atom nuclei [8]. Positive sign H_{eff} on Sn^{119} nuclei in TiCo_2Sn shows that spin density is formed by conduction electrons, most probably, in external s-shells often atoms.

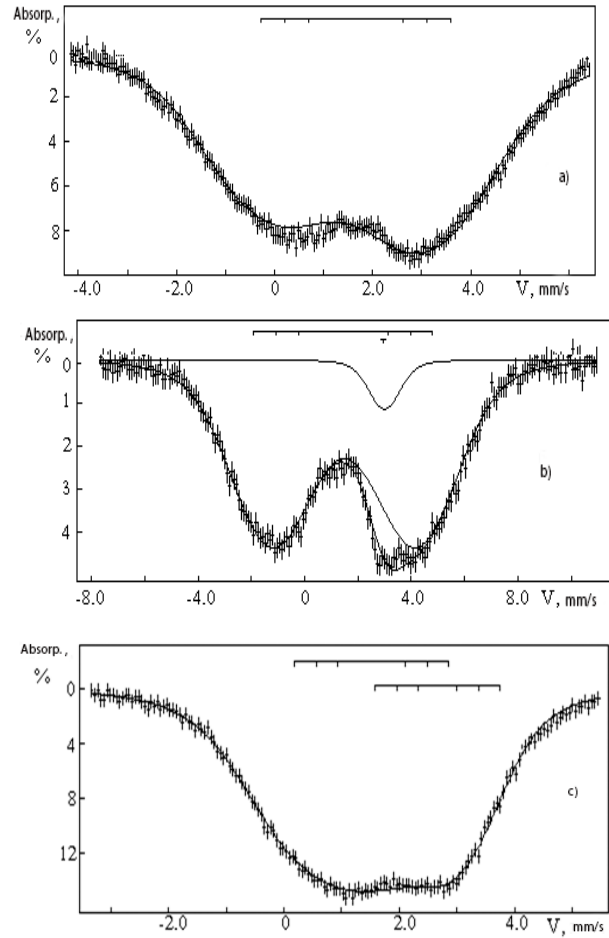


Fig. 3. NGR-spectra of $\text{TiCo}_{2-x}\text{Sn}$ alloys at $T = 80$ K: a) $\text{TiCo}_{1.7}\text{Sn}$; b) $\text{TiCo}_{1.4}\text{Sn}$; c) TiCoSn .

As consistent with the results of our measurements, electric conductivity of alloys TiCoSn and TiCo_2Sn is close. Assuming that concentration of conduction electrons in both alloys is also close, reduction of the number of Co atoms in TiCoSn compared to TiCo_2Sn leads to redistribution of electrons between Co atoms and produces greater occupancy of $3d$ -zone in TiCoSn ,

Table 1

Sn^{119} NGR-spectra parameters in $\text{TiCo}_{2-x}\text{Sn}$ ($x = 0.0 \dots 1.0$).

Alloy	T = 295 K				T = 80 K			
	Sn (1)		Sn (2)		Sn (1)		Sn (2)	
	δ , mm/s	H_{eff} , kOe	δ , mm/s	H_{eff} , kOe	δ , mm/s	H_{eff} , kOe	δ , mm/s	H_{eff} , kOe
TiCo_2Sn	1.41(2)	65/5	-	-	1.44(3)	82.2(5)	-	-
$\text{TiCo}_{1.7}\text{Sn}$	1.51(3)	-	-	-	1.48(2)	28.1(5)	-	-
$\text{TiCo}_{1.4}\text{Sn}$	1.46(2)	-	2.61(3)	-	1.52(3)	50.6(5)	2.99(3)	-
TiCoSn	1.46(2)	-	2.97(2)	-	1.56(3)	19.9(5)	2.99(4)	15.6(8)

Isomer shifts (δ) were determined relative to SnO_2 .

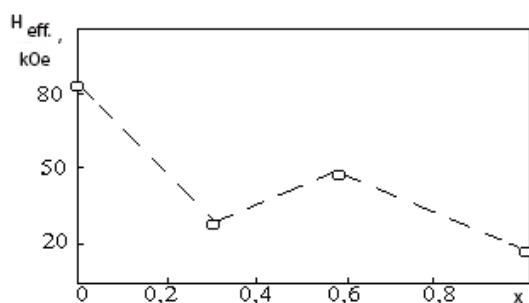


Fig. 4. Dependence of H_{eff} on Sn(1) nuclei for $\text{TiCo}_{2-x}\text{Sn}$ alloys at $T = 80$ K.

which determines reduction of Co atom magnetic moment [9]. Then presence of small values of magnetic fields on tin nuclei in TiCoSn compared to TiCo_2Sn becomes understandable.

Conclusions

Two types of tin atoms Sn (1) and Sn (2) are found in $\text{TiCo}_{2-x}\text{Sn}$ alloys ($x = 0.6$ and 1.0), which are located in crystallographic pyramids and tetrahedral vacancies and which correspond to isomeric shifts of $1.52 - 1.56$ mm/s and 2.99 mm/s. Higher isomeric shear value for Sn (2) atoms compared to Sn (1) atoms indicates higher charge density of s-electrons at Sn (2) nuclei, which may be caused by an increase in the covalence of chemical bonds. Magnetic ordering in $\text{TiCo}_{2-x}\text{Sn}$ alloys is associated with indirect exchange interactions through

polarization of conduction electrons, which in turn lead to the appearance of H_{eff} at the nuclei of non-magnetic tin atoms. A positive sign of H_{eff} on the Sn nuclei in $\text{TiCo}_{2-x}\text{Sn}$ indicates that the spin density is generated by the conduction electrons in the outer shells of tin. Reduction of the number of Co atoms in TiCoSn in equation with TiCo_2Sn leads to the redistribution of electrons between Co atoms and creates the greater occupancy of the $3d$ zone in TiCoSn .

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Особливості кристалічної структури та надтонких взаємодій у сплавах Ti-Co-Sn

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Сплави із загальною формулою $TiCo_2-xSn$ отримували методом спікання первинних компонентів - чистих металів в атмосфері аргону. Сплави гомогенізували відпалом у вакуумованій кварцевій посудині при $T = 1070$ К протягом 500 год. Рентгеноструктурний аналіз підтвердив однофазний стан усіх зразків. Аналіз ядерного гамма-резонансу проводили при $T = 295$ та 80 К з використанням джерела випромінювання $BaSn^{119}Sn$. Встановлено, що атоми Sn у зразках з $x = 0,6$ та $1,0$ знаходяться у двох кристалографічних положеннях, пірамідах (1) і тетраедрах (2), яким відповідають зсуви ізомерів (щодо SnO_2 $1,52 - 1,65$ мм/с для Sn(1) і $2,99$ мм/с для Sn(2)). Розщеплення Зеемана для Sn(1) у $TiCo_2Sn$ відбувається при $T = 295$ і 80 К, а також для композицій з $x = 0,3 - 1,0$ при $T = 80$ К. Для Sn(2) розщеплення Зеемана відзначається лише у сплаві $TiCoSn$ при $T = 80$ К. Зроблено висновок щодо утворення ефективних магнітних полів на немагнітних ядрах атомів олова.

Ключові слова: фази Гейслера, ядерний гамма-резонанс, магнітне поле, ізомерний зсув.