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MÖSSBAUER EFFECT STUDY OF ATOMIC DISORDER IN Fe_2TiSn ALLOY

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Abstract. The Heusler-type alloy Fe_2TiSn was investigated in the temperature range (80-300) K by ^{57}Fe and ^{119}Sn Mössbauer spectroscopy. The purpose of this study was to gain information on the local atomic disorder in this alloy with an emphasis on the hyperfine parameters: magnetic field (B_{hf}) and isomer shift (IS). The first-principle electronic structure calculations based on the tight-binding linearized muffin tin orbital (TB-LMTO) method were performed to get values of hyperfine parameters for ordered and locally disordered Fe_2TiSn alloy. The analysis of ^{57}Fe Mössbauer spectra revealed the existence of an isostructural phase transition at ~240 K, while the analysis of ^{119}Sn Mössbauer spectra provides additional evidence of a change in the atomic magnetic structure near the temperature 200 K.

1. INTRODUCTION

The influence of the local chemical disorder on the magnetic properties of ordered Heusler-type alloys is an intriguing phenomenon. Recently in the series of paper [1-5] was shown that the Heusler Fe_2TiSn alloy belongs to the group of system in which the weakly ferromagnetic and probably heavy fermion behavior is induced by atomic disorder. The Fe_2TiSn crystallize in the $L2_1$-type structure, which consists of four interpenetrating fcc sublattices. Every Fe atom has local tetrahedral symmetry and is surrounded by 4 Ti and 4 Sn atoms. Ti and Sn atoms possess octahedral local symmetry and are surrounded by 8 Fe atoms. The electronic structure LMTO calculations [1, 4] indicated that ordered Fe_2TiSn should be a nonmagnetic semimetal with a pseudogap in the density of states (DOS) at the Fermi level.

The calculations predicted that the stoichiometric compound at equilibrium volume has no magnetic solution, whereas the disordered alloy in which Fe and Ti are intermixed should be magnetically ordered. The electrical resistivity, magnetization and specific heat measurements on the quenched from temperature 1023 K Heusler Fe_2TiSn alloy revealed the occurrence of weak ferromagnetism [1]. At 240 K an abrupt drop in lattice parameter (a) dependence *vs.* temperature was observed and interpreted as evidence of an isostructural phase transition, which is created by an atomic disorder. This drop coincides with unusual features in $\chi(T)$ curve [1]. The inspection of the χ(T) data from 250 K to 350 K leads to a Curie-Weiss law $\chi(T) = C/(T - \theta) + \chi_0$, where $\theta = 250$ K. The X-ray diffraction data of Fe_2TiSn revealed the presence of crystallographic disorder, which is realized by the occupation of the Ti site by Fe in every fifth unit cell [1]. The interaction between such types of "magnetic defects" *via* the long-range Rudderman-Kittel-Kasua-Yosida mechanism may explain the observed weak ferromagnetism.

In the present paper ^{57}Fe and ^{119}Sn Mössbauer spectroscopy was used to investigate an effect of local atomic disorder in Fe_2TiSn. The hyperfine parameters B_{hf} and IS were determined as a function of temperature in the range of (80-300) K. The electronic structure was calculated by LMTO method to gain better understanding of experimental results.

2. EXPERIMENTAL AND CALCULATION DETALS

A Fe_2TiSn ingot was prepared by arc melting the constituent metals on the water-cooled copper hearth in a high-purity argon atmosphere. The sample was annealed at 1073 K for 10 hours and then quenched in water. The ^{57}Fe and ^{119}Sn resonance absorption measurements were carried out using a constant-acceleration spectrometer. A $^{57}CoRh$ (50 mCi) and a $Ba^{119m}SnO_3$ (5 mCi) sources kept at room temperature were used. A palladium foil of 0.25 mm thickness was used as a critical absorber for tin X rays. In all cases, polycrystalline absorbers with thickness ~18 mg/cm^2 were used. The iron and tin Mössbauer spectra were recorded from 80 to 300 K in a liquid nitrogen cryostat. The stability of the sample temperature was about 0.5 K. The special attention was done to the data analysis. The Mössbauer spectra were fitted with a least-squares method program using the Gauss-Legendre technique for evaluation of the transmission integral.

The electronic structure of the ordered compounds was studied by the all-electron self-consistent Linearized Muffin-Tin Orbital (LMTO) method and the calculations were performed using the TB~LMTO-4.7 code [6]. To test the reliability of the approximate TB~LMTO results and to investigate the effect of the Coulomb correlation interaction within the Fe-3*d* band states the electronic structure of the stoichiometric Fe_2TiSn was studied by the general potential (full potential) Linear Augmented Plane Wave (FP-LAPW) method. The calculations were performed using the WIEN2K code [7].

The electronic structure of the F_2TiSn with off-stoichiometric composition and anti-site atom defects was calculated on the supercell with translation vectors (110); ↓ including eight formula units – composition $Fe_{16}Ti_8Sn_8$. Two kinds of defects were analyzed. In the off-stoichiometric composition the excess Fe atom was considered to occupy the nominally Ti position – the composition $Fe_{17}Ti_7Sn_8$. The another considered defect consists of a single pair of Fe and Ti atoms at anti-site positions ($Fe_{AS} \leftrightarrow Ti_{AS}$) – composition $[Fe_{15}Ti_{AS}][Ti_7Fe_{AS}]Sn_8$. In both cases one defect occur per eight unit cells.

The isomer shift was calculated with the use of formula; $IS = \alpha\Delta\rho(0)$, where α is a constant dependent on Mössbauer nuclide type and $\Delta\rho(0)$ is a relative electron density on the nucleus area. In this paper the values: $\alpha = -0.24\ a_0^{-3}$ for ^{57}Fe nucleus [8] and $\alpha = 0.065\ a_0^{-3}$ for ^{119}Sn nucleus [9] were used. A relativistic change $\Delta\rho(0)$ for different compositions has been calculated in relation to the value $\rho(0)$ for α-Fe and metallic Sn at 0 kbar. The isomer shift has been calculated utilizing the electronic charge density $\rho(0)$ taken from the nucleus surface [10]. The hyperfine field B_{hf} affecting the nucleus is superposition of different contributions, but the predominant contribution arises from the Fermi contact interactions. The results for the Fermi contact hyperfine field presented in this paper were calculated by means of the relativistic formula derived by Blügel et al. [11].

3. RESULTS AND DISSCUSION

A. Electronic structure calculations

In the supercell used in the electronic structure calculations, composed with the 8 unit cells of $L2_1$-type, the Fe ↔ Ti intermixing causes, that Fe atom (denoted as Fe0) has the trigonal symmetry and is surrounded by 7 Fe atoms and 1 Ti atom in the first coordination sphere and 6 Sn atoms in the second coordination sphere (Fig. 1). The seven another Fe atoms (denoted as Fe1) have neighborhood (1Fe + 3Ti + 4Sn) in the first coordination sphere. The eighth of the last

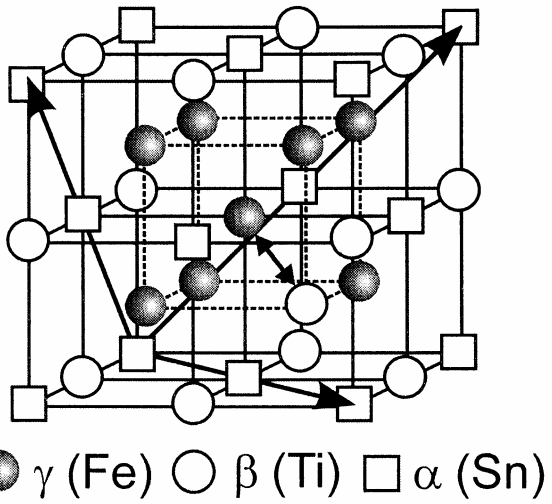

Fig. 1. Atomic environment of the Fe sites in the eightfold supercell with $L2_1$ symmetry. The (↔) arrow shows the direction of Fe-Ti intermixing

iron atoms (denoted as Fe2) have the neighborhood (4Ti + 4Sn). The interesting result which comes from calculations is that redistribution of Fe and Ti atoms in the second coordination sphere of an Fe atom causes very little changes in the values of B_{hf} and IS. The magnetic moment and averaged values of calculated hyperfine parameters for ^{57}Fe nucleus are presented in Table I.

Table I. Magnetic moment μ and averaged values of B_{hf} and IS hyperfine parameters for ^{57}Fe nucleus calculated for $Fe_{16}Ti_8Sn_8$ alloy with a single pair of Fe and Ti atoms at anti-site positions (Fe_{AS} ↔ Ti_{AS})

Atom Fe	Magnetic moment [μ_B]	Isomer Shift [mm/s]	Hyperfine field [kGs]	Population in the supercell
Fe0	2.67	0.18	201.8	1
Fe1	0.3	0.36	40	7
Fe2	0.02	0.38	5	8

The value of IS = 0.41 mm/s (relative to αFe) for ^{57}Fe nucleus in ordered nonmagnetic Fe_2TiSn compound was estimated. The local configuration of the Sn atoms located in the supercell is affected also by Fe ↔ Ti intermixing. The one Ti atom situated in the first coordination sphere of an Sn atom in the ordered $L2_1$ structure causes that a magnetic field with value $B_{hf} \approx 5$ kGs is acted on ^{119}Sn nucleus. However a single Fe atom situated in the second coordination sphere of an Sn atom in $L2_1$ structure increases the value of B_{hf} to ≈ 55 kGs. The value of IS = 1.6 mm/s (relative to $BaSnO_3$) for ^{119}Sn nucleus in ordered nonmagnetic Fe_2TiSn compound and value of IS ≈ 1.7 mm/s for configurations with Fe ↔ Ti intermixing was estimated.

B. ^{57}Fe and ^{119}Sn Mössbauer Study

The ^{57}Fe Mossbauer spectrum of Fe_2TiSn recorded at room temperature is shown in Fig. 2a. A single broad and asymmetric absorption line is observed. When an external magnetic field produced by a rare earth permanent magnet with intensity of 0.42 T is applied, the additional broadening of absorption line is observed, suggesting the presence of a magnetic component

(Fig. 2b). Taking into account results of electronic structure we performed fit to the spectra assuming existence of a magnetic component (Zeeman sextet) that comes from configuration of Fe atoms situated on Ti sites, and a non-magnetic (single line) component arising from ordered bulk.

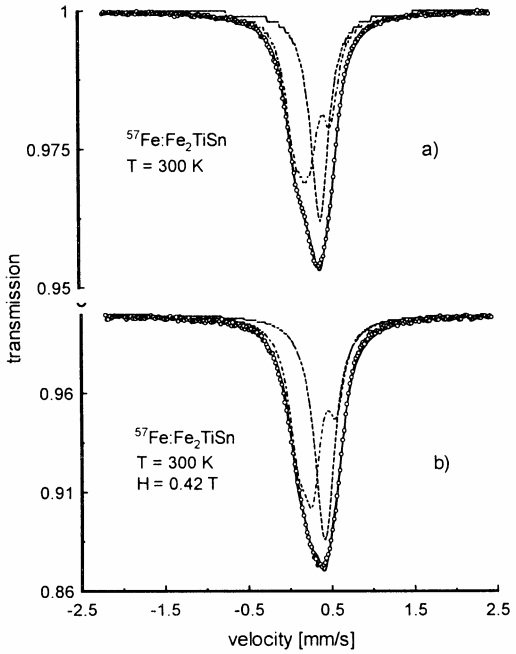

Fig. 2. Mössbauer spectra of ^{57}Fe : Fe_2TiSn measured at room temperature: (a) in zero-applied field, (b) in an external magnetic field of 0.42 T perpendicular to the direction of γ-radiation

For sample measured in zero-applied field and room temperature the following parameters of Zeeman sextet was estimated: hyperfine magnetic field HFM = 10.2 kGs, quadrupole splitting QS = 0.14 mm/s and isomer shift IS = 0.21 mm/s. The isomer shift for single line was IS = 0.35 mm/s. The measurements performed at 80 K and in velocity range appropriate for detecting iron with high magnetic moment (F0 atom) reveal that there are no absorption lines located at $|v| > 1$ mm/s. Although intensity of the high magnetic field component should be small (see Table I), the observed absence of such component in measured spectra indicates that distance between neighboring Fe0 atoms is longer then five lattice constants, in opposition to the results presented in [1].

In the Fig. 4 the temperature dependence of isomer shift for magnetic (IS_M) and non-magnetic (IS_{NM}) components is presented. The two features are interesting. The observed at 240 K a small drop in IS_{NM} curve coincides with observed abrupt drop in the experimental $a(T)$ plot [1]. Although the drop in $IS_{NM}(T)$ is within the errors estimated from the fitting procedure can be interpreted as an evidence of a structural transition in the paramagnetic phase. The transition is probably involved by presence of the monoclinic or orthorhombic deformation of the $L2_1$ structure of the investigated Fe_2TiSn samples. The comparison of the calculated charge density distributions within the unit cells of $L2_1$ and orthorhombic structures have shown that the orthorhombic distortion increases the values of charge densities at nuclei of each constituent atom: +0.39 (a.u.)$^{-3}$ for Sn, +0.17 (a.u.)$^{-3}$ for Fe and +0.06 (a.u.)$^{-3}$ for Ti. It gives the net change in

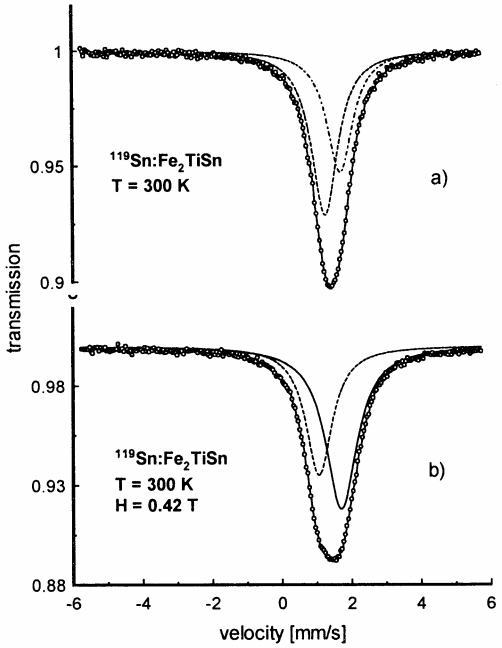

Fig. 3. Mössbauer spectra of ^{119}Sn: Fe_2TiSn measured at room temperature: (a) in zero-applied field, (b) in an external magnetic field of 0.42 T perpendicular to the direction of γ-radiation

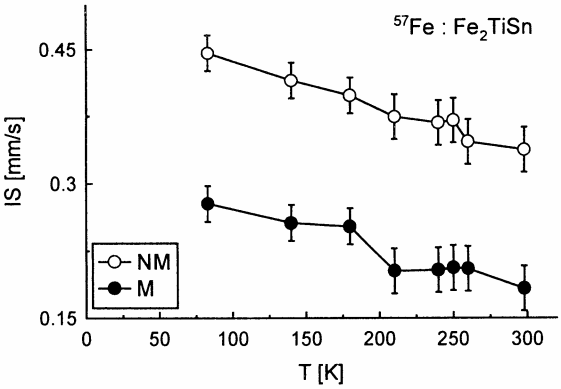

Fig. 4. The temperature dependence of the ^{57}Fe isomer shift for magnetic (M) and non-magnetic (NM) components of Fe_2TiSn Mössbauer spectra. Lines connecting experimental points are added as a guide to the eye

^{57}Fe-IS_{NM} about 0.04 mm/s, with the good relation to experiment. The drop in IS_M curve is shifted to the lower temperatures and is observed in the region near 200 K. It is interesting that this drop coincides with same features in $B_{hf}(T)$ curve, presented on Fig. 5. An increase in B_{hf} at the region of (200-240) K is observed. The physical nature of this behavior is under investigations. Probably a mictomagnetic feature of the specific type of "magnetic defects" which are distributed in disordered Fe_2TiAl alloys is established in this interesting region.

The ^{119}Sn Mössbauer spectrum of Fe_2TiSn recorded at room temperature is shown in Fig. 3a. A single absorption line is observed, which broadening increases in an external field with intensity of 0.42 T (Fig. 3b). Taking into account the features of ^{119}Sn Mossbauer spectroscopy (the thick natural width of the resonant line), it is difficult to perform fitting of the single line spectra with assumption of existence of a magnetic component. We performed deconvolution of

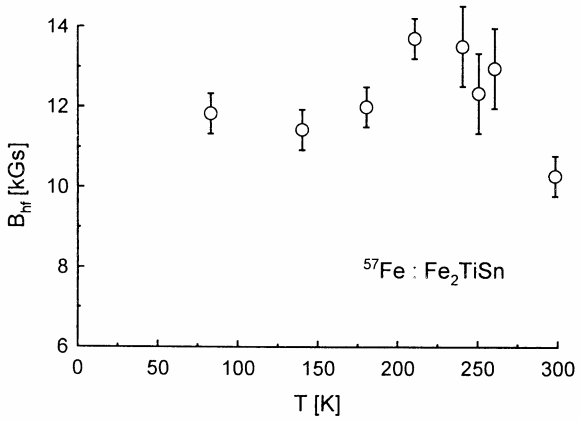

Fig. 5. The temperature dependence of the ^{57}Fe hyperfine magnetic field B_{hf} for magnetic component

^{119}Sn Mössbauer spectra on the two Lorentzian components in the investigated region of temperature (80-300) K. The first one has a stable full widths at half maximum FWHM = 0.95 mm/s. The second Lorentzian line has the IS value in the range (1.66-1.71) mm/s and growing FWHM from 0.92 mm/s at 300 K to 1.34 mm/s at 80 K. The first component can be attributed to the ordered non-magnetic Fe_2TiSn bulk, while the second component to the magnetic clusters produced by Fe ↔ Ti intermixing. The value of 9.2 kGs for B_{hf} acting at ^{119}Sn nucleus at 80 K was estimated from a transmission integral fitting procedure. The values: IS = 1.66 mm/s for magnetic component and IS = 1.52 mm/s for non-magnetic components were determined, with the good accordance to the theoretical ones. The dependence of the area under resonant lines *versus* temperature which correspond to temperature dependence of the Mössbauer absorption probability f' is presented on Fig. 6. A non-linear variation of the ^{119}Sn absorption probability is observed with

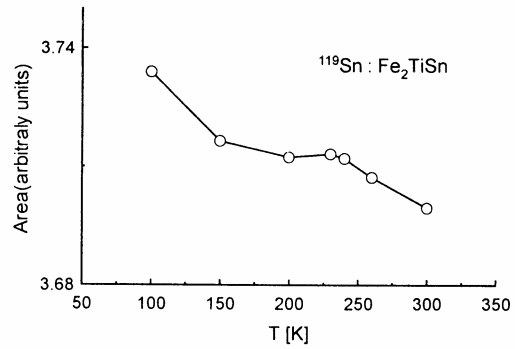

Fig. 6. The area under the ^{119}Sn resonant spectrum of Fe_2TiSn alloy plotted *versus* the temperature. Lines connecting experimental points are added as a guide to the eye

a significant drop at 200 K. It provides additional evidence of a change in the atomic magnetic structure near the temperature 200 K.

4. CONCLUSIONS

The presented results indicate that the Mössbauer spectroscopy is a powerful tool to characterize influence of disorder on the magnetic properties of the Fe_2TiSn alloy. The performed electron

structure calculation and observed at 240 K drop in IS(T) curve for ^{57}Fe nucleus reveals evidence of a structural phase transition in the paramagnetic phase. The analysis of ^{57}Fe and ^{119}Sn Mössbauer spectra provides additional evidence of a change in the atomic magnetic structure near the temperature 200 K. This behavior is probably connected with mictomagnetism of the specific type of "magnetic defects" which are created in disordered Fe_2TiAl alloys due to Fe ↔ Ti intermixing. The values of hyperfine parameters (B_{hf} and IS) obtained from electronic structure calculations are in the good relation to the experimental data.

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