ELECTRONIC STRUCTURE, MAGNETISM
AND HYPERFINE PARAMETERS OF $Fe_{3-x}Ti_xAl$ ALLOYS

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Abstract: The aim of the presented study was to investigate an effect of the alloying on the electronic structure, magnetic and hyperfine properties of Heusler type $Fe_{3-x}Ti_xAl$ alloys. The electronic structure calculations predict the magnetic ground-state of the Heusler Fe_2TiAl with the half-metallic density of states (DOS) in the vicinity of Fermi level (ε_F). The DOS near ε_F has the quasi-gap in the majority spin channel. Applying the super-cell method the electronic and magnetic structure and the hyperfine properties were calculated for wide range of Ti concentration ($0 \leq x \leq 1$). The influence of the local environment on the magnetic hyperfine field on Fe nuclei is discussed.

1. INTRODUCTION

Heusler-type alloys by reason of unique magnetic, thermodynamic and electrical properties are subject to the intensive experimental and theoretical investigations [1-7]. These alloys comprise a class of ternary intermetallic compounds crystallizing in the $L2_1$ type cubic structure. Most of these compounds have ferromagnetic or weak-ferromagnetic properties [3, 6]. Super-paramagnetic properties have been found in off-stoichiometric Fe_2VAl [2]. For some of them the heavy fermion behavior is suggested [3, 8]. For the off-stoichiometric Fe_2VAl alloys the Fe anti-site defects have been proposed as a possible origin of the peculiar thermodynamic and transport properties [7, 9]. Despite intensive investigations some properties of the Heusler-type alloys are still not well understood and constitute a challenging problem.

Resemblance feature in the electronic structure and the semiconductor-like resistance anomaly between Fe_2VAl and Fe_2TiSn has been the to reason search compounds which have similar properties. $Fe_{3-x}Ti_xAl$ has not heretofore been investigated in detail. In the paper we report an *ab initio* investigation of the electronic and magnetic structure, and hyperfine-parameters of $Fe_{3-x}Ti_xAl$.

2. CALCULATION AND RESULTS

The electronic structure calculations have been performed using the Tight Binding Linear Muffin Tin Orbitals (TB-LMTO) method of Andersen et al. [10]. The calculations were scalar relativistic, and did not include the spin-orbit interaction. The exchange-correlation potential was taken within the local spin-density approximation, with the use of a non-local correction to the exchange-correlation potential within the Langreth-Mehl-Hu approximation [11, 12].

The isomer shift for a series of measurement carried out for the same Mössbauer source is usually interpreted with the use of formula [13]; $IS = \alpha \Delta \rho(0)$ whera α is a constant dependent on Mössbauer nuclide type. In this paper, a relativistic change $\Delta \rho(0)$ for different concentration

has been calculated in relation to the value of $\rho(0)$ for α-Fe at 0 kbar. The isomer shift has been calculated utilizing the electronic charge density from the nucleus surface [14].

The hyperfine field B_f affecting the nucleus constitutes the superposition of three different contributions (Fermi contact, orbital and dipolar [13]) but the predominant contribution to the total hyperfine field is from the Fermi contact interaction. 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. [15].

The stoichiometric Fe_2TiAl crystallizes in the $L2_1$ crystal structure and belongs to the class of so called full-Heusler compounds with the general chemical formula X_2YZ. X and Y are the transition d-metal ($3d$ or $4d$) atoms or $4f$ Rare Earth ones, while Z is the sp-element (e.g. Al, Si or Sn). In the $L2_1$-type unit cell of X_2YZ Z atoms form the unit cell of the fcc-type lattice in which further two equivalent positions [(1/4 1/4 1/4); (3/4 3/4 3/4)] (γ-sites) are occupied by X atoms and one position (1/2 1/2 1/2) (β-site) is occupied by Y atom. The X^γ atoms have the tetrahedral coordination with four Z and four Y^β atoms as nearest neighbors, while the octahedral coordination of Y^β atoms consists of eight X^γ atoms in the first coordination sphere. In the $Fe_{3-x}Ti_xAl$ alloys ($x < 1$) the excess Fe atoms were assumed to replace the Ti^β atoms and with eight surrounding Fe^γ atoms form the nine-Fe cluster.

For the purpose of the alloying simulations we have performed the calculations with the use of the super-cell including eight formula units. For Ti concentrations $x = 0, 0.125, 0.25, 0.5, 0.625, 0.75, 0.875, 1$ different configurations of the Fe at nominally Ti^β positions (hereafter called as Fe-anti-site (Fe-AS) or Fe^β atoms) were tested and the site preference have been established. The preferred configurations were chosen those with the minimal total energy. Calculations have shown that for a given Ti-concentration the total energy differences between the optimal and remaining configurations amount roughly to 0.05-5 eV per formula unit. For each energetically preferred configuration the unit cell parameter was determined from the volume optimization procedure.

Electronic and magnetic structure results are summarized in Figures 1 and 2. Figure 1 shows the changes in the total density of states (DOS) upon increasing contents of titanium in the $Fe_{3-x}Ti_xAl$ structure. From the detailed analysis of the partial densities of states it has been found that DOS near the Fermi energy is dominated by the minority spin DOS of the Fe^γ atoms. With increasing concentration of titanium this Fe^γ-$d_\downarrow$ band shifts almost rigidly to the lower energy, giving rise to the simultaneous decrease of the local magnetic moments of the Fe^γ atoms. The quasi-gap in the minority spin DOS located above this band goes closer to the Fermi energy and in the stoichiometric Fe_2TiAl becomes the true energy-gap of 0.2 eV width. In the majority spin DOS the sharp peak located at binding energy of 1 eV is composed of hybridized d-states of the both Fe^γ and Fe^β atoms. This band is separated from the rest of the majority spin DOS by the sharp dips located at the both sides of the band. With decreasing number of Fe^β atoms the peak shifts closer Fermi energy and its magnitude decreases. In the end-compound Fe_2TiAl it disappears definitely leaving the quasi-gap located just at the ε_F giving rise to the semi-metallic character of the Fe_2TiAl DOS

Figure 2 shows the partial atomic magnetic moments on different constituent atoms (part (a)) and average magnetic moment per formula unit (part (b)) versus Ti concentration. The magnetic moment of Fe^β atoms is stable within (2.4-2.6) μ_B range and robust against the Ti contents.
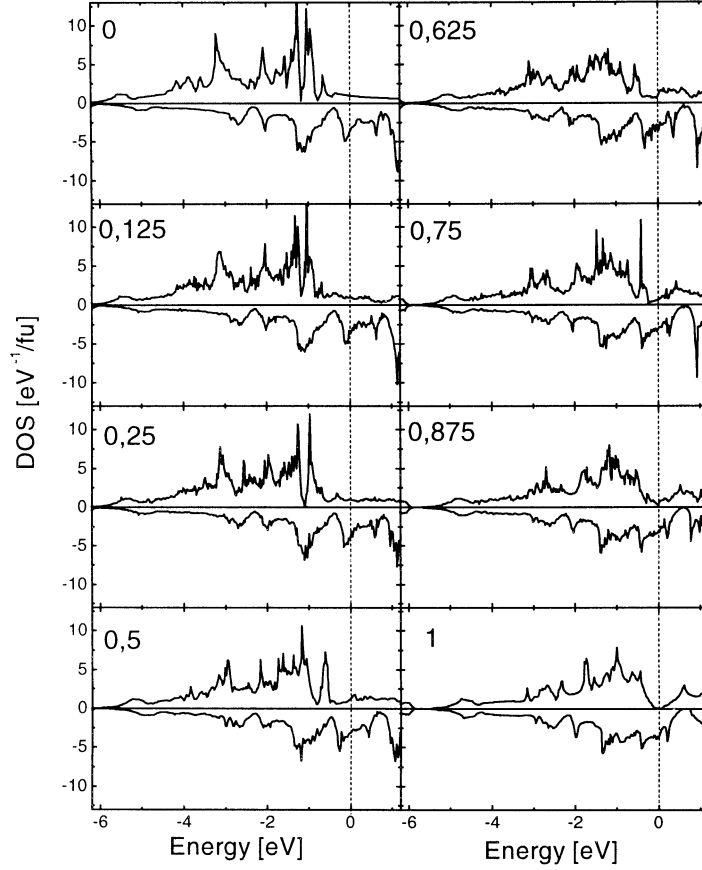
Fig. 1. Spin resolved total density of states for Fe$_{3-x}$Ti$_x$Al series with different Ti concentrations. The vertical dash lines show the Fermi energy position. The negative DOS presents the minority-spin states

The eight iron atoms neighboring the Fe$^\beta$ one, strongly polarized for $0 < x < 0.5$, lose their magnetic polarization for higher concentrations. In the stochiometric Fe$_2$TiAl the magnetic moment of Fe$^\gamma$ atom is ~0.7 μ_B. The Ti partial moment is polarized oppositely to the iron moments and its magnitude of 0.32 μ_B in Fe$_2$TiAl grows slightly with decreasing Ti contents as the system magnetization increases.

The total magnetic moment falls down almost linearly with increasing Ti concentration (Fig. 2b). For the Fe$_2$TiAl calculations predict $M_{tot} = 1$ μ_B/fu in accordance with the phenomeno-logical Slater-Pauling formula $M_{tot} = Z_v - 24$ established for the magnetic *full*-Heusler compounds [6] (Z_v is the generalized valence of the formula unit [6], and for Fe$_2$TiAl $Z_v = 2 \times 8 + + 4 + 3 = 23$). The calculated factor of the M_{tot} *versus* Ti concentration linear relation shown in Fig. 2b was found equal -6.2 μ_B while the estimated from the Slater-Pauling formula is equal

-4 μ_B. The discrepancy may be due to the non-zero magnitude of Ti-local moments antiparallel to the unit cell magnetic moment.
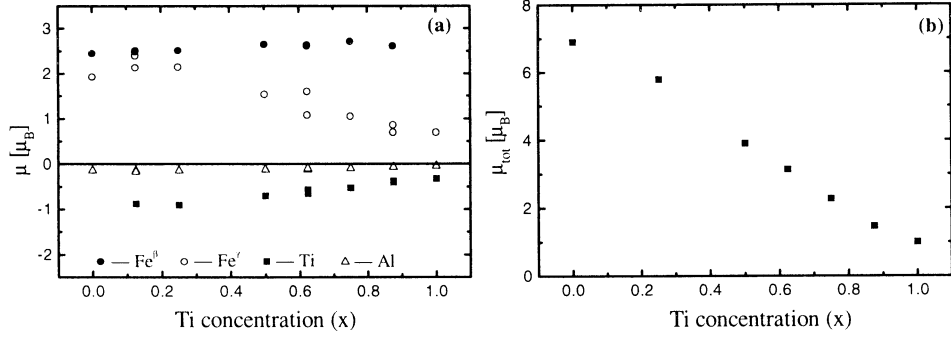

Fig. 2. Partial atomic – (a) and average per formula unit – (b) magnetic moments *versus* Ti concentration in $Fe_{3-x}Ti_xAl$
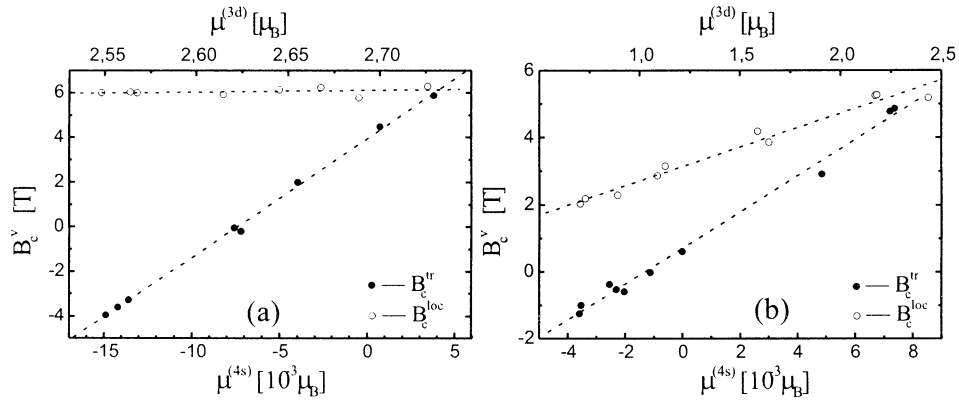

Fig. 3. Decomposition of the valence hyperfine field into the and contributions shown *versus* respectively $\mu^{(3d)}$ and $\mu^{(4s)}$ partial moments for Fe^{β} – (a) and Fe^{γ} – (b) atoms

The Fermi contact hyperfine field (B_c) is dominated by the core electron contribution (B_c^c). Its magnitude scales linearly with μ_{3d} moment of iron atoms with the scaling factor of order of -12 T/μ_B for both types iron atoms. Non-negligible valence electron contributions (B_c^v) are of opposite sign to the B_c^c ones and their magnitude are less than 10 T.

The B_c^v contribution can be decomposed into the *local valence* (B_c^{local}) and *transferred* (B_c^{tr}) parts [16, 17]. The both components of the B_c^v can be estimated from the formula $B_c^v = B_c^{loc} + B_c^{tr} = \alpha \times \mu_{4s} + \beta \times \mu_{3d}$. Figure 3 shows the results of the splitting. The B_c^{loc} part scales linearly with μ_{3d} moments of Fe atoms. The positive scaling factors was calculated to (1-2) T/μ_B. The scaling factor of the B_c^{tr} (μ_{4s}) linear relation was found of order of 540 T/μ_B (close to previously calculated values [16-18]).
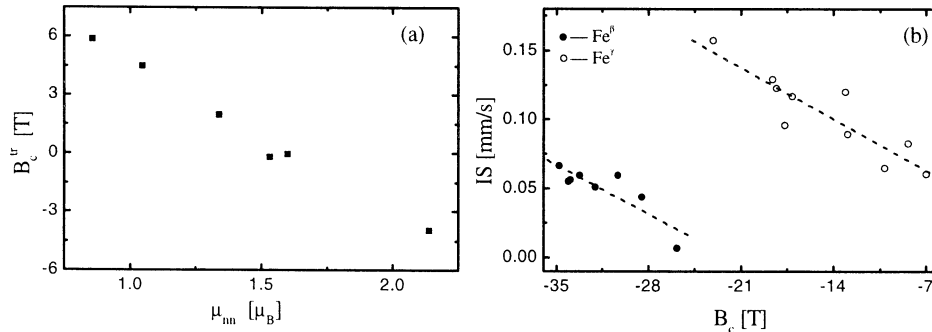
Fig. 4. a) Dependence of the *transferred* hyperfine field on the average magnetic moment of the first coordination sphere of Fe^β atoms. b) Correlation between the Fermi contact hyperfine field and isomer shift for Fe^β and Fe^γ atoms

The sign and magnitude of the B_c^{tr} part is driven by the magnetic structure of the local environment of the Mössbauer probe iron. For the Fe^β atoms, surrounded by the eight magnetic Fe^γ atoms and isolated from the rest of the structure by the nonmagnetic Al and Ti atoms, it was possible to find the linear relation between the B_c^{tr} and an average magnetization of the atoms forming the first coordination sphere (Fig. 4a). Because of the complicated variation of the magnetic neighborhood of the Fe^γ atoms no correlation between the *transferred* hyperfine field and local environment magnetic properties can be established.

Figure 4b shows correlation between the total Fermi contact hyperfine field and isomer shift. A similar effect but for the average B_c and IS value had already been observed by Frąckowiak [13] for the Fe-Al compounds with $B2$ structure. Within a phenomenological model [13] the changes in spin density of the Fe atoms are directly related to that of charge density.

3. CONCLUSIONS

The Fe_2TiAl is of weak ferromagnetic character with the total magnetic moment satisfying the Slater-Pauling relation. The DOS shows half-metallic character with quasi-gap in the majority spin channel centered at Fermi level. The true energy-gap is found above Fermi energy in the minority DOS. The excess Fe atoms at nominally Ti sites are strongly polarized magnetically and give rise to the narrow band inside the pseudo-gap of majority spin DOS. The intensity of the related peak of the DOS grows and its position shifts to lower energies with increasing Fe contents. For one type of Fe atoms the linear dependence of the *transferred* hyperfine filed on the local environment average magnetic moment has been established. An interesting correlation between hyperfine field and isomer shift has been found for both types of Fe atoms in the $Fe_{3-x}Ti_xAl$ series which physical nature is under investigation.

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