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**Citation style:** Michalecki Tomasz, Deniszczyk Józef, Frąckowiak Janusz E.  
(2004). First principles study of the isomer shift in Fe<sup>44</sup>M<sub>6</sub>A<sub>150</sub>  
(M=Ti,V,Cr,Co,Ni,Cu) alloys with B2 structure. "Nukleonika" (Vol. 49, suppl.  
3 (2004), s. 3-6).



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# First principles study of the isomer shift in $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$ ( $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Co}, \text{Ni}, \text{Cu}$ ) alloys with B2 structure

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**Abstract** The  $^{57}\text{Fe}$  isomer shift for  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  intermetallics with the B2 structure doped with  $\text{M} = \text{Ti}, \text{V}, \text{Cr}, \text{Co}, \text{Ni}$  and  $\text{Cu}$  additions has been calculated with the tight-binding linear muffin-tin orbital (TB-LMTO) method. The effect of variation of Wigner-Seitz (WS) spheres radii on the calculated equilibrium lattice parameter ( $a$ ) and isomer shift (IS) was analyzed. The calculations have shown that the  $^{57}\text{Fe}$  isomer shift in  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  intermetallics is directly proportional to the changes in the local  $4s$  electronic charge at Fe atoms involved by M additions. The screening effect of  $4s$  electrons due to changes in ( $4p + 3d$ ) electronic charge is of secondary importance. The calculated dependence of the average IS on nuclear charge ( $Z$ ) of the alloying metal (M) follows qualitatively the tendency observed experimentally for the M impurities in the Fe host.

**Key words** iron • aluminum • isomer shift • Fe-Al compound • LMTO

## Introduction

The intermetallic compounds with the B2 structure have been extensively studied with emphasis on their rich variety of magnetic and structural properties [4, 5, 16]. The B2-structured FeAl compound is seen as a candidate material for elevated temperature structural applications because of its good oxidation resistance, low density and relatively low cost [9]. Although FeAl is ductile at high temperatures, the mechanical properties can be improved by transition metal ternary additions which, replacing iron, influenced on hardness and defect morphology [12]. Additionally, alloying elements can affect the electron distribution and bonding character in intermetallic materials [6].

In this work, we determine the  $^{57}\text{Fe}$  isomer shift of FeAl doped in Fe sublattice by the most promising and most frequently investigated additions such as transition Ti, V, Cr, Co, Ni and Cu metals. Based on the first principle calculations within the constructed super-cell including 16 atoms (eight B2-type formula unit), in which the central Fe atom is replaced by an M atom, we evaluate the average value of isomer shift (IS) and changes in IS caused by M impurities situated in 2nd and 3rd coordination sphere of an Fe atom. Since the M-impurity replaces the Fe atom in the ordered FeAl with the B2-type structure, it enters only the second and more distant coordination spheres centered at Fe sites. We have shown that the effect of impurities on  $^{57}\text{Fe}$ -IS in  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  compounds with the B2 structure depends on the nuclear charge  $Z$  of M atom and its distance from the Mössbauer nuclide (in an oscillating manner).

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Received: 6 July 2004, Accepted: 10 September 2004

## Method of calculations

The calculations were performed using the tight-binding linear muffin-tin orbital method (TB-LMTO) [2]. The local spin-density approximation of the exchange-correlation potential (XC) was taken in the form given in [3] with a non-local correction described in [8, 10].

The electronic structure of the  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  compounds has been calculated using the super-cell methodology of alloy modeling. In the calculations we considered the cubic super-cell consisting of eight unit cells of underlying the B2 structure ( $2 \times 2 \times 2$  super-cell, 16 atoms).

The  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  composition was simulated by appropriate replacing the one central Fe atom by an M atom in the super-cell. The general effect of such substitution is lowering of the space group symmetry, which leads to the splitting of atomic positions into crystallographically non-equivalent Fe subgroups. Table 1 summarizes the compositions of the first three coordination spheres for different types of iron atom at non-equivalent positions in the super-cell. It is worth to notice that  $\text{Fe}_0$  atom whose neighborhood is nominally the same as in FeAl, has  $6\text{Fe}_1$  and  $12\text{Fe}_2$  atoms in the second and third coordination sphere, respectively.

Volume optimizations have shown that for small concentrations of M impurities the lattice parameter changes negligibly as compared to that of FeAl. Based on this observation we assumed the lattice parameter for all investigated alloys is the same as for FeAl compound ( $a_0 = 5.53$  a.u.).

Within the standard approach the isomer shift is usually interpreted with the use of formula:  $\text{IS} = \alpha\Delta\rho(0)$  [13], where constant  $\alpha$  depends on the Mössbauer nuclide type (for the  $^{57}\text{Fe}$   $\alpha = -24a_0^{-3}$ ) and the  $\Delta\rho(0)$  is the electronic charge density difference at the center of Mössbauer nuclide in the absorbent and the standard material (in our case the  $\alpha\text{-Fe}$  in the equilibrium volume). For the reasons described in our previous paper [11], instead of using charge density at the center of nucleus we apply the electronic charge densities at nucleus surface.

The TB-LMTO method utilizes the atomic sphere approximation (ASA) [2] according to which the atoms within the unit cell are modeled by the Wigner-Seitz (WS)

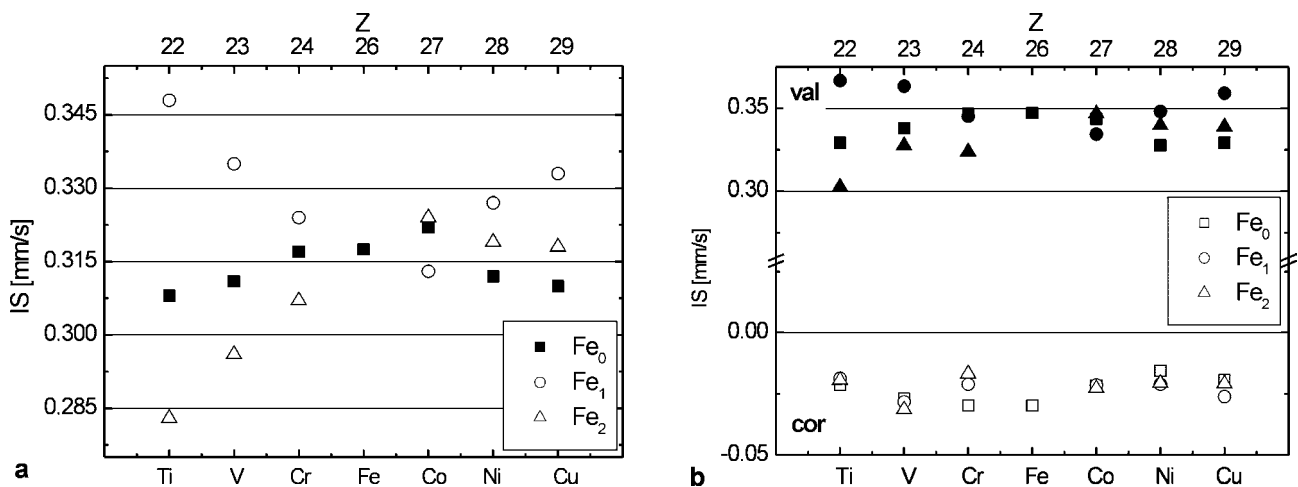
**Table 1.** Composition of the first three coordination spheres of the non-equivalent Fe atoms in a super-cell including 16 atoms ( $8 \times \text{B2}$  formula unit).

	Atom	1st sphere	2nd sphere	3rd sphere
$\text{Fe}_{44}\text{M}_6\text{Al}_{50}$	$\text{Fe}_0$	8Al	$6\text{Fe}_1$	$12\text{Fe}_2$
	$\text{Fe}_1$	8Al	$2\text{Fe}_0 + 4\text{Fe}_2$	$4\text{M} + 8\text{Fe}_1$
	$\text{Fe}_2$	8Al	$2\text{M} + 4\text{Fe}_1$	$4\text{Fe}_0 + 8\text{Fe}_2$

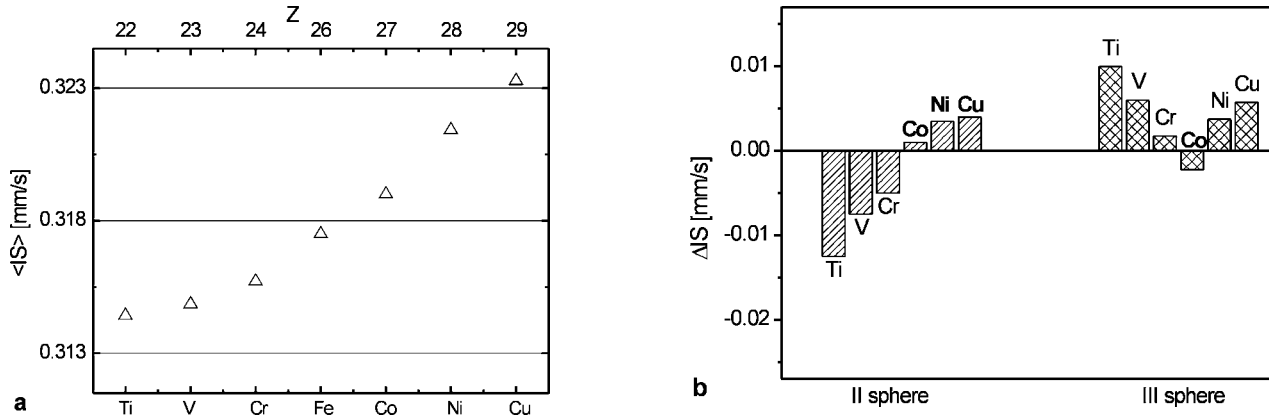
atomic spheres. The choice of the WS radii can influence the results of electronic structure calculations. To resolve this problem we apply two methods of setting the WS radii in FeAl calculations. The first one consists in keeping constant the Fe-WS radius (taken from the equilibrium volume  $V_{\text{eq}}$  calculated for elemental  $\alpha\text{-Fe}$ :  $4/3\pi(r_{\text{WS}}^{\text{Fe}})^3 = 1/2V_{\text{eq}}$ ) and calculation of the Al-WS radius from the volume equation [2]. In the second method the radii of the WS-spheres were taken so as to fulfill the volume equation [2] and to give the closest values of the potential at the surfaces of WS spheres of different atoms. The much better agreement with the experimental isomer shift for FeAl was obtained for the WS-radii chosen according to the second method and these ones were applied in all presented calculations.

## Results and discussion

In Fig. 1a we present the calculated values of isomer shift for different types of iron atoms in  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$ . A non-local changes of IS can be observed for the  $\text{Fe}_0$  atom whose neighborhood corresponds nominally to that of Fe in FeAl, however with different types of Fe atoms in the second and third coordination sphere. The results for  $\text{Fe}_0$  have shown, that except for Co, ternary additions in  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  system cause the increase of the  $s$ -type charge density at  $\text{Fe}_0$  atoms, in relation to non disturbed  $\text{Fe}_0$  atoms in the FeAl compound. The local changes in IS involved by impurities placed in the 2nd and 3rd coordination sphere of Fe atom, depend on the nuclear charge  $Z$  of impurity M and its distance from iron atom. The strongest influence is



**Fig. 1.** Isomer shift (a) and core (cor) and valence (val) contributions (b) calculated for different types of iron atom in  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  compounds.



**Fig. 2.** Average  $^{57}\text{Fe}$  isomer shift (a) and  $\Delta \text{IS}$  changes of isomer shift involved by impurities situated in 2nd and 3rd coordination sphere (b) for  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  compounds.

observed for impurities having the  $Z$  smaller than Fe atom. These located in the second coordination sphere of Fe atom ( $\text{Fe}_2$ -type) lowers the IS value in relation to the FeAl compound. The opposite effect is observed for impurities placed in the third coordination sphere ( $\text{Fe}_1$ -type). In this case, an increase in IS value is observed. The impurities situated on the right-hand side of Fe in the periodic table only slightly are influencing the IS value. Comparison of the partial core and valence contributions of the IS calculated for different types of Fe atoms (Fig. 1b) shows that the changes in IS are mainly caused by the variation of  $4s$  charge density involved by the alloying additions. The effect of alloying on the core contribution of IS is of minor importance [1].

The average value  $\langle \text{IS} \rangle$  of isomer shift has been calculated with the use of formula:  $\langle \text{IS} \rangle = \sum_t n_{\text{Fe}}^{(t)} \cdot \text{IS}_{\text{Fe}}^{(t)} / n_{\text{Fe}}$ , where:  $n_{\text{Fe}}^{(t)}$  denotes the multiplicity of type  $t = (0, 1, 2)$  of Fe atom (Table 1);  $\text{IS}_{\text{Fe}}^{(t)}$  are the calculated values of isomer shift and  $n_{\text{Fe}}$  is the number of Fe atoms in the super-cell. Figure 2a shows the dependence of  $\langle \text{IS} \rangle$  versus nuclear charge  $Z$  of ternary additions  $M$ . The continuous increase in  $\langle \text{IS} \rangle$ , from Ti addition to Cu addition, is observed and follows the changes in IS calculated for the  $3d$ -impurities in dilute Fe alloys [1]. A negative (positive) difference ( $\langle \text{IS} \rangle_{\text{FeMAI}}^{(\text{Fe})} - \langle \text{IS} \rangle_{\text{FeAl}}^{(\text{Fe})}$ ) means that the charge density  $\rho(0)$  at the Fe nucleus has increased (decreased). These changes in  $\langle \text{IS} \rangle$  (Fig. 2a) can be explained in terms of electronegativity arguments according to which the electron charge flows from the element with lower electronegativity to the one with higher electronegativity [1] (in our case:  $\text{Ti, V, Cr} \rightarrow \text{Fe}$  and  $\text{Fe} \rightarrow \text{Co, Ni, Cu}$ ).

The experimental results for the  $^{57}\text{Fe}$ -IS are often interpreted with the use of the following linear formula:  $\text{IS} = \text{IS}(0) + \sum_i n_i \cdot \Delta \text{IS}_i$ , where:  $\text{IS}(0)$  is the non-local contribution;  $\Delta \text{IS}_i$  are the local changes of IS due to the single impurity located at the  $i$ th coordination sphere and  $n_i$  is the number of  $M$ -atoms in the  $i$ th coordination sphere. Figure 2b shows the local changes of the isomer shift on Fe nucleus,  $\Delta \text{IS}_i = (\text{IS} - \text{IS}(0)) / n_i$ , where  $\text{IS}(0) = \text{IS}(\text{Fe}_0)$ . The figure demonstrates that the transition element additions  $M = (\text{Ti, V, Cr})$  in  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  compounds give rise to the oscillations of  $s$ -type charge density around impurity which result in the oscillating sign of  $\Delta \text{IS}$  for Fe atoms located in the second and third coordination sphere of  $M$ -atom. For the  $M = (\text{Co, Ni, Cu})$  transition elements

the sign of  $\Delta \text{IS}$  is practically the same for 2nd and 3rd coordination sphere and only for Co element a reversion is observed.

Although the IS measures only the change of the charge density of  $s$ -type electrons at the Fe nucleus, indirectly it reflects also the changes of charge density of electrons with the  $p$  and  $d$  orbital character. To answer the question how the changes of the partial charges  $\Delta n_s$ ,  $\Delta n_p$  and  $\Delta n_d$  correlate with the variation of the IS we analyze the linear relation  $\text{IS} = A \cdot \Delta n_s + B \cdot \Delta n_{p+d}$ , where  $A$  and  $B$  are fitted constants. In the formula the  $\Delta n_l$  ( $l = s, p + d$ ) denote the relative changes of charge (charge transfer) of  $s$ , and  $(p + d)$ -type electrons at the Fe atom in  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  compounds with respect to the corresponding charges at Fe atom in FeAl. A similar relation between the isomer shift and charge transfers is accepted view about the isomer shifts in metallic alloys [1, 13–15]. Akai *et al.* [1] used the formula:  $\Delta \rho(0) = C(\Delta n_s + R \cdot \Delta n_d)$  where  $R$  term describes the reduction of the valence  $s$  charge density at the origin due to the increase of the  $d$  electron number. In our formula the parameter  $B$  describes the effectiveness of the valence  $p$  and  $d$  electrons in “screening out” the  $4s$  charge density at the Fe nucleus. The values of the  $A$  and  $B$  parameters resulting from the fitting of the proposed linear relation to the calculated IS for different types of Fe atoms in  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  are listed in Table 2. The values of  $A$ , when transformed to the  $C$  constant, agree very well with those reported in [1]. The calculations of Akai *et al.* [1] for transition metal impurities in dilute Fe alloys yield  $R = -0.06$ , while our calculations give the values of  $R$  in the range  $(-0.02 \text{ to } -0.05)$ .

The negative  $A$  corresponds to the increase of the charge density at Fe nucleus caused by the increasing amount of  $4s$  charge in the Fe nucleus. The positive and one order of magnitude smaller value of the  $B$  parameter than that of the  $A$  one points that the effectiveness of the

**Table 2.** Results of fitting for proportionality parameters  $A$  and  $B$ .

Atom	A	B
$\text{Fe}_0$	-1.883	+0.063
$\text{Fe}_1$	-2.477	+0.051
$\text{Fe}_2$	-1.521	+0.082

$pd$ -screening for the isomer shift is much less than the  $4s$  charge transfers.

## Conclusions

To summarize, we note that our calculations reflect the trends in the variation of the  $^{57}\text{Fe}$  isomer shift observed experimentally in the FeAl alloyed with the transition metal elements [7] and that obtained from the calculations reported for transition metal impurities in the  $\alpha$ -Fe host [1]. We have shown that the isomer shift for iron aluminides doped with transition metal elements in Fe site is directly proportional to the changes of the local  $4s$  and ( $4p + 3d$ ) charge, but the effectiveness of the ( $p$ ) $d$  screening is small. Moreover, the  $M = \text{Ti, V}$  and  $\text{Cr}$  atoms located in the second and third coordination sphere of an Fe atom in  $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$  compounds give rise to the oscillations  $s$ -type charge density which results in the oscillating sign of  $\Delta\text{IS}$  contribution to isomer shift. The local changes  $\Delta\text{IS}$  of isomer shift for ternary additions with almost filled  $3d$  orbitals show no oscillatory behavior. The estimated range ( $-0.02 \div -0.05$ ) of  $R$ -factor which describes the effectiveness of the  $d$  electrons in screening the  $s$  electrons is in the good accordance with value calculated by Akai *et al.* [1].

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