



You have downloaded a document from
RE-BUŚ
repository of the University of Silesia in Katowice

Title: First principles study of the isomer shift in Fe⁴⁴M₆A₁₅₀
(M=Ti,V,Cr,Co,Ni,Cu) alloys with B2 structure

Author: Tomasz Michalecki, Józef Deniszczyk, Janusz E. Frąckowiak

Citation style: Michalecki Tomasz, Deniszczyk Józef, Frąckowiak Janusz E. (2004). First principles study of the isomer shift in Fe⁴⁴M₆A₁₅₀ (M=Ti,V,Cr,Co,Ni,Cu) alloys with B2 structure. "Nukleonika" (Vol. 49, suppl. 3 (2004), s. 3-6).



Uznanie autorstwa - Użycie niekomercyjne - Bez utworów zależnych Polska - Licencja ta zezwala na rozpowszechnianie, przedstawianie i wykonywanie utworu jedynie w celach niekomercyjnych oraz pod warunkiem zachowania go w oryginalnej postaci (nie tworzenia utworów zależnych).



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

Tomasz Michalecki,
Józef Deniszczyk,
Janusz E. Frąckowiak

Abstract The ^{57}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 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}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}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}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).

T. Michalecki[✉], J. Deniszczyk, J. E. Frąckowiak
Institute of Materials Science,
University of Silesia,
12 Bankowa Str., 40-007 Katowice, Poland,
Tel.: +48 32/ 359 17 76, Fax: +48 32/ 259 69 29,
e-mail: tmichalecki@o2.pl

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 Fe_0 atom whose neighborhood is nominally the same as in FeAl, has 6Fe_1 and 12Fe_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 α depends on the Mössbauer nuclide type (for the ^{57}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
$\text{Fe}_{44}\text{M}_6\text{Al}_{50}$	Fe_0	8Al	6Fe_1	12Fe_2
	Fe_1	8Al	$2\text{Fe}_0 + 4\text{Fe}_2$	$4\text{M} + 8\text{Fe}_1$
	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_{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 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 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 Fe_0 atoms, in relation to non disturbed 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

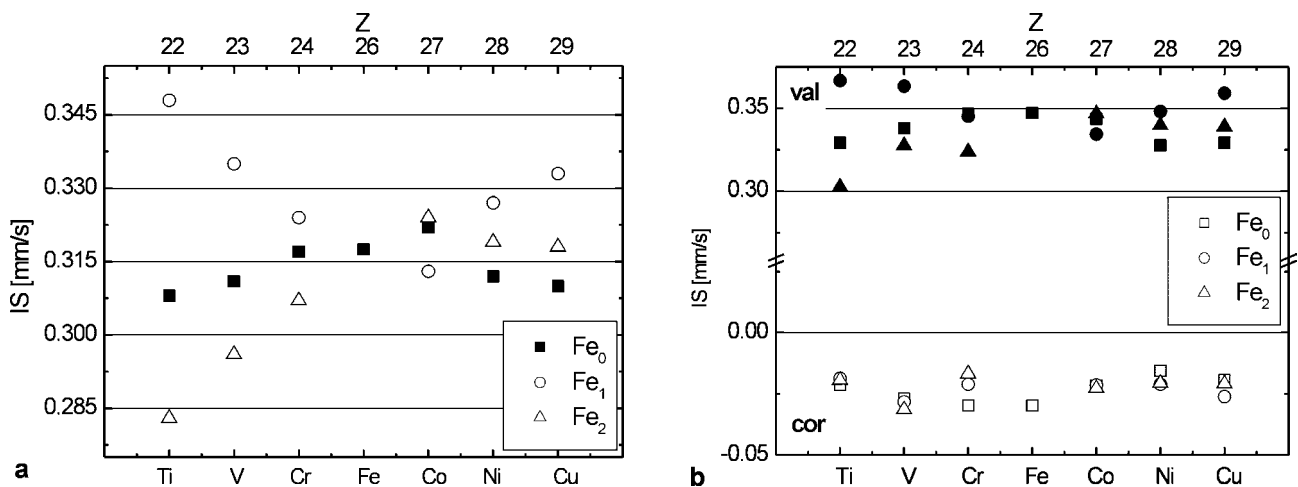


Fig. 1. Isomer shift (a) and core (cor) and valence (val) contributions (b) calculated for different types of iron atom in $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$ compounds.

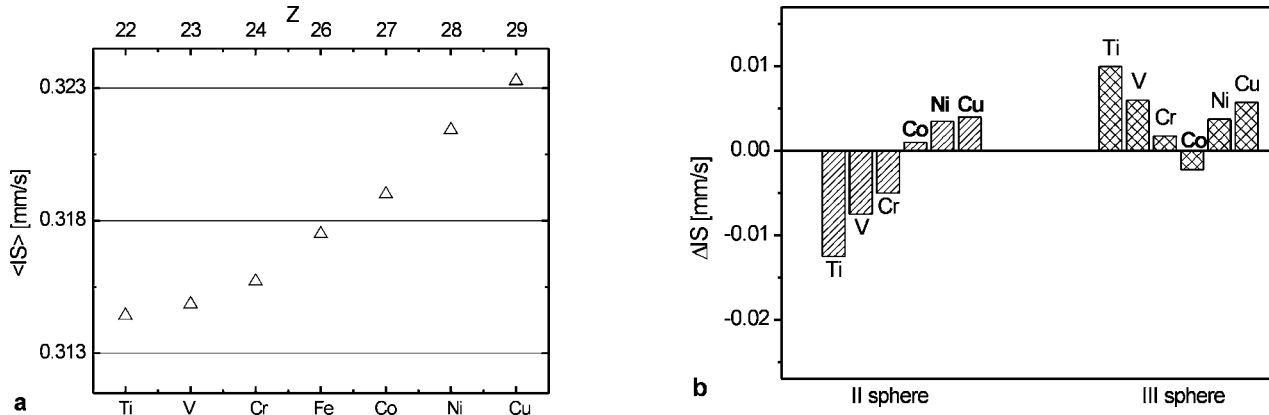


Fig. 2. Average ^{57}Fe isomer shift (a) and ΔIS changes of isomer shift involved by impurities situated in 2nd and 3rd coordination sphere (b) for $\text{Fe}_{44}\text{M}_6\text{Al}_{50}$ compounds.

observed for impurities having the Z smaller than Fe atom. These located in the second coordination sphere of Fe atom (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 (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_{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}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; ΔIS_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 $\text{M} = (\text{Ti, V, Cr})$ 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 ΔIS for Fe atoms located in the second and third coordination sphere of M-atom. For the $\text{M} = (\text{Co, Ni, Cu})$ transition elements

the sign of ΔIS 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 Δn_s , Δn_p and Δn_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 Δn_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
Fe_0	-1.883	+0.063
Fe_1	-2.477	+0.051
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}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 α -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 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 ΔIS contribution to isomer shift. The local changes ΔIS 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].

References

1. Akai H, Blüggel S, Zeller R, Dederichs PH (1986) Isomer shifts and their relation to charge transfer in dilute Fe alloys. *Phys Rev Lett* 56:2407–2410
2. Andersen OK, Jepsen O, Glötzel D (1985) Canonical description of the band structures of metals. In: Bassani F, Fumi F, Tosi MP (eds) *Highlights of condensed matter theory*. Elsevier, Amsterdam, North-Holland, pp 59–179
3. Barth V, Hedin L (1972) A local exchange-correlation potential for the spin polarised case. *J Phys C: Solid State Phys* 5:1629–1635
4. Bogner J, Steiner W, Reissner M *et al.* (1998) Magnetic order and defect structure of $\text{Fe}_x\text{Al}_{1-x}$ alloys around $x = 0.5$: An experimental and theoretical study. *Phys Rev B* 58:14922–14933
5. Botton GA, Guo GY, Temmerman WM, Humphreys CJ (1996) Experimental and theoretical study of the electronic structure of Fe, Co, and Ni aluminides with the B2 structure. *Phys Rev B* 54:1682–1691
6. Fu CL, Zou J (1996) Site preference of ternary alloying additions in FeAl and NiAl by first-principles. *Acta Mater* 44:1471–1478
7. Hanc A, Frąckowiak JE (2004) Defect structure of Fe-Al and Fe-Al-X ($X = \text{Ni; Cu; Cr}$) metallic powders obtained by the self-decomposition method. *Nukleonika* 49;S3:s7–s11
8. Hu CD, Langreth DC (1985) A spin dependent version of the Langreth-Mehl exchange-correlation functional. *Phys Scripta* 32:391–396
9. Jordan JL, Deevi SC (2003) Vacancy formation and effects in FeAl. *Intermetallics* 11:507–528
10. Langreth DC, Mehl MJ (1981) Beyond the local-density approximation in calculations of ground-state electronic properties. *Phys Rev B* 28:1809–1834
11. Michalecki T, Deniszczyk J, Frąckowiak JE (2003) *Ab initio* study of the effect of pressure on the hyperfine parameters of ^{57}Fe in bcc phase. *Nukleonika* 48;S1:s45–s48
12. Munroe PR, Kong CH (1996) The effect of ternary additions on vacancy hardening in near stoichiometric FeAl. *Intermetallics* 4:403–415
13. van der Woude F, Sawatzky GA (1974) Mössbauer effect in iron and dilute iron based alloys. *Phys Rep* 12:335–374
14. Watson RE, Bennett LH (1978) Comment on volume-corrected isomer shifts of transition-metal impurities. *Phys Rev B* 17:3714–3717
15. Watson RE, Swartzendruber LJ, Bennett LH (1981) Bonding effects in dilute transition-metal alloys. *Phys Rev B* 24:6211–6220
16. Zou J, Fu CL (1995) Structural, electronic, and magnetic properties of 3d transition-metal aluminides with equiatomic composition. *Phys Rev B* 51:2115–2121