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Ab Initio Study of the ^{57}Fe Electric Field Gradient in $(FeAl)_{1-x}T_x$ (T = $3d$ Element) Dilute Alloys with B2-Type Structure

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We present an *ab initio* study of the electric field gradient at Fe nuclei in the series of $(FeAl)_{1-x}T_x$ dilute alloys with $B2$-type crystal structure. The ternary additions T, of concentration $x \approx 0.06$, from the group of $3d$-type transition metals (Ti, V, Cr, Mn, Co, Ni, Cu) are considered. Lattice, local valence electron ($3d$, $4p$) and weakly bound $3p$ core electron contributions to electric field gradient are separated out and discussed in the context of the T-atom site preference and changes of the electronic structure upon alloying. Contrary to earlier reports, we found that for most Fe nuclei the dominant contribution comes from the d-type valence electrons cancelled partially by the $3p$ and $4p$ electric field gradients which are both of opposite sign to that of the $3d$ one. The shielding effect of $3p$ semicore electrons is found and related to the electric field gradient contributed by the local valence electrons.

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1. Introduction

The Fe–Al based intermetallic compounds and alloys with the $B2$-type structure, although studied for decades, are still a subject of both theoretical and experimental investigations, due to their high temperature applications. It is well known that the stoichiometric ordered FeAl phase is hard to obtain, and furthermore the FeAl compound shows low ductility at higher temperatures [1]. Experimental investigations have proven that the transition-metal additions to the Fe–Al system

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can improve greatly the most important properties of base FeAl alloy [1]. Defect structures and ordering processes in Fe–Al based $B2$-type intermetallic alloys are decisive for their properties. The Mössbauer spectroscopy, which is one of the methods capable of measuring the local atomic arrangement, is often used to study the defect structure of the alloys. However, because of atomic disorder, the precise assignment of hyperfine interaction parameters (isomer shift (IS), hyperfine magnetic field, and electric field gradient (EFG)), and consequently the unique analysis of the Mössbauer spectra is difficult. The interpretation of the Mössbauer spectra can be made easier when aided by *ab initio* all electron quantum computations which yield the precise information on the local electronic charge and spin distribution for a given local atomic arrangement.

In our theoretical investigations, we considered the transition $3d$ elements (T = Ti, V, Cr, Mn, Co, Ni, and Cu) as single dilute additions in otherwise ordered FeAl compound of $B2$-type structure. In a previous paper, we reported the self-consistent band-structure calculations for ternary $(FeAl)_{1-x}T_x$ ($x \approx 0.06$) systems [2]. We considered different locations of T atoms in the FeAl lattice (i.e. replacing the Fe or Al atoms) and performed the site preference analysis. For the structures with the T atoms at preferred sites, the magnetic properties, IS and magnetic hyperfine field (B_{hf}) were determined [2] by means of the approximate tight-binding linear muffin-tin orbitals method [3]. We have recalculated IS and B_{hf} using more exact full-potential linearized augmented plane wave (FP-LAPW) method, but the results obtained did not differ substantially from those presented in [2] so now we focus on the investigations of the electric field gradient alone. The aim of our present study was to determine, by *ab initio* methods, the dependence of electric field gradient at Fe nuclei in $(FeAl)_{1-x}T_x$ on the type of T atom located at preferred sublattices. We have found that even for a given location of T atom (e.g. at Al sublattice — as for the T-additions with atomic number $Z < 26$) — the hyperfine parameters strongly depend on the type of T atom. Separation of the electronic states of Fe into three different groups: core — $1s$, $2s$, $2p$; intermediate — $3s$, $3p$, and valence — $3d$, $4s$, allows analysis of different partial contributions to the hyperfine parameters. We have found that weakly bound $3p$ core states of Fe atom participate significantly in EFG at Fe-nucleus and their contribution follows the Sternheimer law for shielding effect [4]. We compare the calculated results with the available experimental data.

2. Computational details

The electronic structure calculations were performed using the WIEN2k code of Schwarz et al. [5] employing the general FP-LAPW method based on the density functional theory (DFT) formalism. The gradient corrected local spin density approximation (LSDA) for the exchange correlation (XC) potential was used in the form developed in [6]. The core electronic states were partitioned into true core states ($1s$, $2s$, $2p$ for Fe) which were treated atomic-like in the self-consistent

muffin-tin (MT) spherical potential, and weakly bound semicore states ($3s$, $3p$ for Fe) considered as local orbitals (LO) [7] and treated in the full (nonspherical) potential. For the core states, the fully relativistic DFT formalism was employed, while for the valence and LO states the scalar-relativistic approximation neglecting the spin–orbit interaction is used.

In the FP-LAPW method, the unit cell is divided into non-overlapping MT spheres (centered at the atomic sites) and an interstitial region. The results of EFG calculations are sensitive to the MT radii, the calculations for the almost touching MT spheres have shown that the EFG values can change by few percent. To eliminate the effect of unphysical dependence of EFG on MT radii, we have chosen the same values of MT radii (2 a.u.) for all atomic specious, independent of structure composition. The set of the k vectors was established to achieve the total energy error less than 10^{-6} Ry. Presented calculations were performed for lattice parameters evaluated from the total energy minimization procedure [2].

To handle the fractional T-atom concentration in $(FeAl)_{1-x}T_x$, the super-structures were used, constructed on the basis of the supercell with eight FeAl formula units, spanned by the doubled translation vectors of the base FeAl unit cell. Within the superstructure considered for T atoms located at Al sublattice, the positions of eight Fe atoms are crystallographically equivalent and possess the $3m$ local point symmetry. The nearest T-atom locates at the first coordination sphere of Fe. In case of the T-atoms located at the Fe-sublattice, the remaining seven Fe-atoms in the superstructure are all surrounded by eight Al-atoms in the first coordination sphere and divide into three crystallographically inequivalent groups. For the first one, with the cubic $m3m$ site symmetry, the T-atoms locate at the 5th coordination sphere. Second group is formed by three Fe-atoms (named Fe_1) with the $4/mmm$ site symmetry and the nearest four T-atoms in the 3rd coordination sphere. The last group consists of three Fe-atoms (named Fe_2) with the $4/mmm$ site symmetry and the nearest two T-atoms located in the 2nd coordination sphere. We are aware that the considered local atomic configurations do not exhaust all possible in real $(FeAl)_{1-x}T_x$ alloys. However, we claim that for the ordered FeAl matrix and for low T-atom concentration the considered configurations, with the T-atoms at preferred sites, are most probable.

The quadrupole splitting (QS) is an effect of interaction of nuclear quadrupole moment with an electrostatic potential characterized by the nonzero-valued EFG tensor. Within the *ab initio* electronic structure calculation methods, based on DFT, the resulted electronic charge distribution function, besides the total energy, is the key physically reliable quantity. Solution of the Poisson equation for this charge distribution allows to determine the electrostatic potential at any point of the crystal. Weinert [8] has shown that for the shape model of periodic charge distribution used in the FP-LAPW method, the analytic solution of the Poisson equation yields the main component (ϑ_{zz}) of the EFG tensor at central nucleus in the form

$$\vartheta_{zz} \propto \frac{4\pi}{5} \int_0^{R_t} \frac{\rho_{20}(r)}{r^3} r^2 \mathrm{d}r - \frac{4\pi}{5} \int_0^{R_t} \frac{\rho_{20}(r)}{r^3} \left(\frac{r}{R_t}\right)^5 r^2 \mathrm{d}r$$
$$+ 4\pi \sum_{\boldsymbol{K}} V(\boldsymbol{K}) j_2(K R_t) Y_{20}(\hat{K}), \tag{1}$$

where R_t is the atomic MT radius, $V(\boldsymbol{K})$ represents the Fourier component of electrostatic potential outside MT sphere, the j_2 and Y_{20} are the second order Bessel and spherical harmonic functions, respectively. The (2,0) spherical component of the electronic charge density inside the muffin-tin sphere of the atom in question, defined as

$$\rho_{20}(r) = \sum_{\varepsilon_{nk} < \varepsilon_F} \sum_{l,m} \sum_{l',m'} R_{lm}(\varepsilon_{nk}; r) R_{l'm'}(\varepsilon_{nk}; r) G_{2ll'}^{0mm'} \tag{2}$$

is determined by the radial wave functions $R_{lm}(E_{nk}; r)$ of all non-core electronic states with an energy up to the Fermi energy ε_F inside the MT sphere (the $G_{Lll'}^{Mmm'}$ denotes the Gaunt coefficient). The formula (1) for ϑ_{zz} is utilized in the WIEN2k code [9].

The main component of EFG tensor (1) divides in contribution of electrons located inside MT sphere (first term) and the part dependent on the charge distributed outside the MT sphere (last two contributions). Calculations for metallic elements have shown that the second and last terms of (1), called *lattice* EFG [9], contribute very weakly to ϑ_{zz} and the first term coming from the local electronic charge density (valence and semicore) dominates. The structure of ρ_{20} (2) allows one to analyze separately contributions to ϑ_{zz} of states located at different regions of energy scale and for different sets of (l, l') orbital quantum numbers. Within approximations used in the calculations, the contribution to EFG of deep true core states is omitted, but as argued in [9, 10], their contribution to ϑ_{zz} is negligible. The investigations reported in [9, 11] for the series of hcp metals and some iron compounds have proven that the procedure of calculations based on formula (1) give the results in very good agreement with experimental data.

3. Results and discussion

The dependence of total ϑ_{zz} on kind of the T element in $(\mathrm{FeAl})_{1-x}\mathrm{T}_x$ is shown in Fig. 1. Due to the site symmetry of Fe atoms the asymmetry factor of EFG tensor equals zero for all considered positions of Fe. Variation of the ϑ_{zz} reflects the reconstruction of the electronic charge density due to formation of the bonds between central Fe atom in question and surrounding atoms. For the T-atom additions with atomic number $Z < 26$, which prefer the Al-sublattice, the highest value of ϑ_{zz} is found for composition with T = Cr for which also the smallest lattice parameter was obtained [2]. It can indicate that the addition of Cr-atoms to the FeAl structure enhances the interatomic binding in $\mathrm{FeAl}_{1-x}\mathrm{Cr}_x$ alloy. For the T-atom additions with atomic number $Z > 26$, which locate preferably in Fe-sublattice, two groups of Fe-atoms, Fe_1 and Fe_2, show opposite polarization of ϑ_{zz}. This indicates different orientation of the dominating binding orbitals at
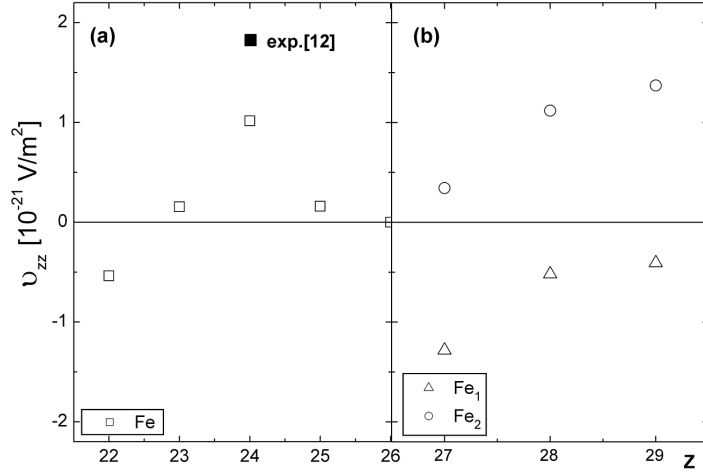
Fig. 1. Dependence of the ϑ_{zz} at Fe nuclei on the type of T-atom addition in $(FeAl)_{1-x}T_x$ series. The results for superstructures with T-atoms at preferred sites are presented only.

Fe$_1$ and Fe$_2$ sites, i.e. along the z-axis for Fe$_1$ ($\vartheta_{zz} < 0$) and within the xy plane for Fe$_2$ ($\vartheta_{zz} > 0$). This kind of disorder of binding orbitals on different types of Fe-atoms in $Fe_{1-x}T_xAl$ (T = Co, Ni, Cu) series can be responsible for the larger value of lattice parameters obtained for these compounds [2].

The quantitative results for ϑ_{zz} at Fe nuclei with separated partial contributions are collected in Table. In the series of investigated compounds, the lattice contributions to the EFG at Fe nuclei (ϑ_{zz}^{lat}), given by the difference between the ϑ_{zz}^{tot} and ϑ_{zz}^{val+LO} (Table), are small (few percent) comparing to the local contributions. The only exception is $FeAl_{1-x}Mn_x$ structure where ϑ_{zz}^{lat}, though very small (-0.03×10^{-21} V/m^2), exceeds 20% of total EFG. The symmetry of the $G_{2ll'}^{0mm'}$ coefficient in (2) causes that — for the single electron basis set limited to the s, p, d and f states — the nonzero contributions to local part (ϑ_{zz}^{val+LO}) of ϑ_{zz} are only possible for the (p, p), (s, d), (d, d), (p, f) and (f, f) sets of (l, l') orbital quantum numbers. Our calculations confirmed previously reported observations [9] that the (s, d), (p, f) and (f, f) contributions are small due to spherical symmetry of s-type charge density and minutely small number of f-type electrons in the system.

The variation of the EFG at Fe nuclei across the series of investigated alloys is driven by the changes in asphericity of the charge density inside the Fe MT sphere of the valence $3d$, $4p$ electrons and those occupying the weakly bound $3p$ shell. In contrary to the calculations reported for the hcp transitions metals [9], a comparison of the partial $\vartheta_{zz}^{val:pp}$, $\vartheta_{zz}^{val:dd}$ and $\vartheta_{zz}^{LO:pp}$ contributions listed in Table shows that, with some exceptions, the ϑ_{zz} at Fe nuclei is dominated by $d-d$ contribution. The p-electron contributions ($3p$ and $4p$) are both of opposite sign with respect to that of d-electrons and compensate partially the $d-d$ part (except

Values of lattice ($\vartheta_{zz}^{\text{lat}}$) and the local electron part ($\vartheta_{zz}^{\text{val+LO}}$) with separated dominant partial contributions ($\vartheta_{zz}^{\text{val}:pp}$, $\vartheta_{zz}^{\text{val}:dd}$, $\vartheta_{zz}^{\text{LO}:pp}$) of electrons occupying respectively the valence $4p$, $3d$, and $3p$ local orbital states, and the quadrupole splitting (QS) calculated for ^{57}Fe nuclides in $(\text{FeAl})_{1-x}\text{T}_x$ structures with T-atoms located at preferred sublattices.

T atom	Fe nuclide	$\vartheta_{zz}^{\text{lat}}$	$\vartheta_{zz}^{\text{val+LO}}$	$\vartheta_{zz}^{\text{val}:pp}$	$\vartheta_{zz}^{\text{val}:dd}$	$\vartheta_{zz}^{\text{LO}:pp}$	QS ($\eta = 0$)
		[10^{21} V/m^2]					[mm/s]
Ti	Fe	0.007	−0.532	−0.181	−0.264	−0.075	−0.117
V	Fe	−0.014	0.160	−0.673	1.242	−0.398	0.034
Cr	Fe	0.028	1.020	−0.930	2.628	−0.684	0.222
Mn	Fe	−0.032	0.159	−0.669	1.352	−0.529	0.035
Co	Fe$_1$	−0.001	−1.282	0.134	−1.642	0.229	−0.280
	Fe$_2$	0.007	0.343	0.545	−0.344	0.138	0.075
Ni	Fe$_1$	0.002	−0.519	0.425	−1.094	0.156	−0.113
	Fe$_2$	0.028	1.120	1.883	−1.209	0.443	0.245
Cu	Fe$_1$	0.006	−0.412	0.744	−1.367	0.219	−0.089
	Fe$_2$	0.044	1.327	2.865	−2.191	0.662	0.299

the case of Ti). In case of Fe$_2$ atoms in Fe$_{1-x}$T$_x$Al structures (where T-atoms locate in the Fe sublattice) the positive $\vartheta_{zz}^{\text{val}:pp}$ even dominates and determines the sign of total EFG. The change of sign of $p-p$ and $d-d$ contributions across the $(\text{FeAl})_{1-x}\text{T}_x$ series occurring when the site preferred by T-atom changes is related to the change of the local site symmetry of Fe position.

The valence electron contribution to the EFG at Fe nuclei in $(\text{FeAl})_{1-x}\text{T}_x$ is a result of changes in the electronic band structure forced by the ternary T-atom in the FeAl structure. Its presence influences the band structure of FeAl in several ways. First, because of the difference between the electronic configuration and atomic radii of T-atom and the replaced atom, the T-atom leads to a modification of the symmetry and strength of local crystal potential. This, in turn, removes the degeneracy and changes energies of the p- and d-type states belonging to the neighboring Fe-atoms. As a result, the population of the partial p- and d-type orbitals in the MT sphere of Fe atoms becomes asymmetric, leading to the axial polarization of the corresponding electronic charge densities. Furthermore, the change of the location in the band structure of the partial Fe p- and d-type states modifies the hybridization interaction they participate in, which can strongly modify their orbital character and influence their spatial charge distribution. Detailed analysis of the partial densities of states confirmed such an effect. Some traces of these effects can be seen in Fig. 2, which presents the total, spin polarized density of states of all compounds studied. We found also that — because of the strong spin polarization of the density of states at the Fermi level in all investigated com-
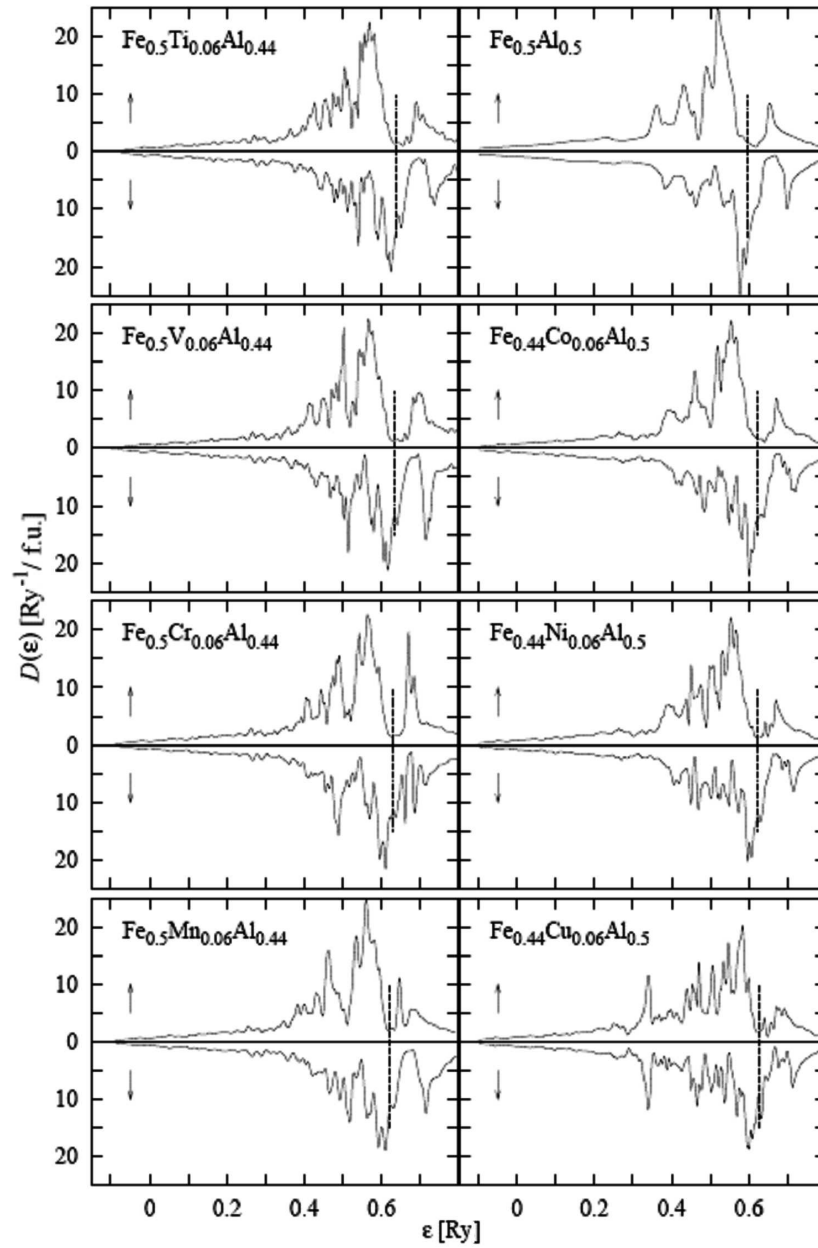
Fig. 2. Spin polarized total density of states calculated for the series of $(FeAl)_{1-x}T_x$ compounds with the T-atoms located at the preferred sublattices.

positions (Fig. 2) — the valence electron contribution to ϑ_{zz} is spin-dependent. Furthermore, we observe that for both spin polarizations the valence contribution is sensitive to the local magnetic moment of Fe atom.

Marathe and Trautwein [13] have introduced a simple model which relates the partial p- and d-type contributions to the valence part of EFG with the asymmetry in the partial orbital populations described by the functions: $\Delta n_p = (1/2)(n_{p_x} + n_{p_y}) - n_{p_z}$ for p-type electrons and $\Delta n_d = n_{dx^2} + n_{dxy} - (1/2)(n_{dxz} + n_{dyz}) - n_{dz^2}$ for the d-type. The application of the appropriate formulae given in [13] leads in our case to a qualitative agreement between the shape of Z-dependence of the estimated values of EFG and those shown in Fig. 1, but the magnitudes of both results differ significantly. Especially for the p-type valence electrons, the model gives strongly underestimated contribution to EFG.

In many attempts to explain EFG basically from the value of $\vartheta_{zz}^{\text{lat}}$ obtained within the point charge model, the traditional equation was used in the form [4]:

$$\vartheta_{zz} = (1 - \gamma_\infty)\vartheta_{zz}^{\text{lat}} + (1 - R)\vartheta_{zz}^{\text{local}}, \tag{3}$$

where γ_∞ and R relate, respectively, to the antishielding and shielding effects, which yield the polarization of charge density of atomic electrons bound by the nucleus in question.

In our *ab initio* approach, the local orbital contribution to EFG can be associated with the second term of Eq. (3). According to our results the changes of $\vartheta_{zz}^{\text{LO}:pp}$ also correlate with those of valence electron contribution, but the correlation is not as simple as given in (3). Instead we have found the linear relation

$$\vartheta_{zz}^{\text{LO}:pp} = a_p \vartheta_{zz}^{\text{val}:pp} + a_d \vartheta_{zz}^{\text{val}:dd}. \tag{4}$$

Fitting of the formula (4) to the partial ϑ_{zz} values listed in Table gives the coefficients a_p and a_d equal to 0.146 and –0.179, respectively. It is evident that the polarization of the $3p$ electronic charge density enhances the $\vartheta_{zz}^{\text{val}:pp}$ contribution (kind of antishielding effect) and diminishes the $\vartheta_{zz}^{\text{val}:dd}$ part (shielding effect). The explanation of the phenomena lies in the relative position of the $3p$ charge density maximum with respect to that of $3d$ and $4p$ electrons [4].

4. Summary

We have studied the electric field gradient at Fe nuclei in the series of $(\text{FeAl})_{1-x}\text{T}_x$ ternary dilute ($x = 0.06$) alloys with $B2$ type crystal structure. We have shown that both the sign and magnitude of EFG depends on the type of ternary addition. Calculations have shown that the dominant contribution to EFG comes from the $3d$ valence electrons of Fe atom. The shielding effect of $3p$ semicore states has been found and described.

Acknowledgments

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