

## EFFECT OF THE LOCAL ENVIRONMENT ON THE ELECTRONIC AND MAGNETIC PROPERTIES OF $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$ AND $\text{Fe}_{3-x}\text{Cr}_x\text{Si}$

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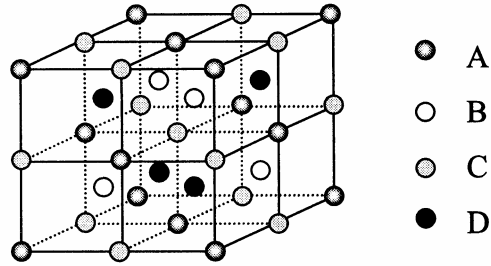
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**Abstract:** The effect of the local environment on formation of local magnetic moments in  $\text{Fe}_3\text{Si}$  and  $\text{Fe}_3\text{Al}$  substituted by chromium is examined using self-consistent spin-polarised TB-LMTO method. An influence of the local environment on the distribution of local magnetic moments, hyperfine magnetic fields is discussed. Results of calculations confirmed that the presence of chromium atom in the nearest neighbourhood causes strong fall of the hyperfine field on Fe as well decrease of magnetic moment of Fe in (A, C) and B sites.

### 1. INTRODUCTION

$\text{Fe}_3\text{Si}$  and  $\text{Fe}_3\text{Al}$  alloys doped with transition metal atoms were investigated many times by different experimental [1-13] and theoretical techniques [14-18]. Both  $\text{Fe}_3\text{Si}$  and  $\text{Fe}_3\text{Al}$  crystallise in  $\text{DO}_3$ -type structure (Fig. 1). This structure can be described as four interpenetrating face-centred cubic Bravais lattices originated at (0, 0, 0), (1/4, 1/4, 1/4), (1/2, 1/2, 1/2) and (3/4, 3/4, 3/4) positions and abbreviated as A, B, C, and D, respectively. In the perfectly ordered compound aluminium or silicon atoms occupy D positions. There are two non-equivalent types of iron in (A, C) position and in B position. One of them – B position has eight Fe nearest neighbours in an octahedral configuration, the second one – (A, C) site – is surrounded by four Fe and four Si or Al atoms for  $\text{Fe}_3\text{Si}$  and  $\text{Fe}_3\text{Al}$  respectively. Transition metal atoms preferentially occupy one type of these sites, depending of their positions in the Periodic Table of Elements [3]. Atoms of elements that are placed on the left-hand side of iron preferentially locate at B-sites; atoms to the right-hand side of iron demonstrate strong preference for (A, C) positions in  $\text{DO}_3$ -type structure. The aim of paper is to investigate an influence of the local surrounding of iron on its magnetic moment, hyperfine field and density of states in compounds where iron is substituted by chromium. The chromium concentration in both of alloys changes in range from  $x = 0$  to  $x = 0.5$ . Particular interest in this alloys stems from the experimental observation indicating that chromium in  $\text{Fe}_3\text{Si}$  does not obey the aforementioned simple rule of preferential substitution [1-2, 6-10].

In order to test an influence of the local environment on electronic and magnetic properties of  $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$  and  $\text{Fe}_{3-x}\text{Cr}_x\text{Si}$ , magnetic effects connected with all possible configurations in the nearest neighbour's shell for Fe(A, C) and Fe(B) sites were analysed. In the case of a few Zeeman sextets, the results can be compared with the ones obtained from Mössbauer experiments [1, 2, 7-9]. The presence of chromium atom in the nearest neighbourhood causes strong

Fig. 1. The  $DO_3$ -type structure

decrease of the magnetic moment and hyperfine field on iron. The total magnetic moments as well as the magnetic moments of chromium and iron were shown to decrease almost linearly with the concentration of chromium in considered alloys [17-18].

## 2. METHOD OF CALCULATIONS

The electronic structure and magnetic properties were calculated within the framework of the local spin density approximation (LDA) by the spin-polarized self-consistent tight-binding linearized muffin-tin orbital method (TB-LMTO) in the atomic sphere approximation (ASA) [19] for the experimental values of the lattice constant [6, 10]. Calculations were carried out for the exchange correlation potential in the form of von Barth and Hedin [20]. The Langreth-Mehl-Hu non-local exchange-correlation [21] was added. The calculations were performed for at least 250 k-points in the irreducible wedge of the Brillouin zone. The Fermi contact contribution to the hyperfine field discussed in this paper was determined by the spin density at the position of the nucleus of the examined atom [22]:

$$B = \frac{8}{3} \pi \mu_B [\rho_{\uparrow}(0) - \rho_{\downarrow}(0)]$$

where  $\mu_B$  is the Bohr magneton, and the term in brackets is the electronic spin density at the iron nucleus. In present calculation the supercell structure with 32 atoms in the cell was used. The supercell structure can be divided into 32 simple cubic sublattices. Eight of them are occupied by Si or Al atoms (D positions), whereas Fe and Cr randomly occupy the remaining sublattices (A, B, C positions). However, in reality a weak disorder between B and D sublattices in  $Fe_3Si$  – based alloys [2] and furthermore between [A, C] and D in  $Fe_3Al$  – based alloys [8] is observed experimentally.

## 3. RESULTS

The calculated hyperfine fields and the local magnetic moments at Fe atoms in (A, C) and B sites for  $Fe_{3-x}Cr_xAl$  and  $Fe_{3-x}Cr_xSi$  (where  $x = 0, 0.125, 0.25, 0.375, 0.5$ ) are presented in the Table I. In the whole range of concentration of chromium all possible atomic configurations of the nearest neighbour shell of Fe at (A, C) and B positions are specified. A few percent occupation of D-sites by Fe atoms, observed in some experiments [2, 8] in studied alloys, is neglected in present consideration. Both, the position of Fe atom in the unit cell and the nearest neighbour shell configuration, influence the local magnetic moment. Since the number of magnetic nearest neighbours of Fe on (A, C) positions is two times smaller than

around B sites, the magnetic moment of Fe(A, C) is also smaller than the magnetic moment of Fe(B). The magnetic moment of Fe(A, C) is found to be below  $1.6 \mu_B$  and  $2.0 \mu_B$  for  $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$  and  $\text{Fe}_{3-x}\text{Cr}_x\text{Si}$ , respectively. The moment of Fe(B) is above  $2.0 \mu_B$  in both compounds.

Table I. Hyperfine magnetic fields and the local magnetic moments for  $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$  and  $\text{Fe}_{3-x}\text{Cr}_x\text{Si}$

Concentration $x$	Position of Fe atom	Nearest neighbour atomic configuration (K = Al or Si for $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$ and $\text{Fe}_{3-x}\text{Cr}_x\text{Si}$ ), respectively	$\text{Fe}_{3-x}\text{Cr}_x\text{Al}$		$\text{Fe}_{3-x}\text{Cr}_x\text{Si}$	
			Magnetic moment [ $\mu_B$ ]	Calculated hyperfine field [T]	Magnetic moment [ $\mu_B$ ]	Calculated hyperfine field [T]
0	(A, C)	{4Fe(B), 4K(D)}	1.857	26.900	1.415	21.750
	B	{8Fe(A, C)}	2.396	32.782	2.615	32.012
0.125	(A, C)	{4Fe(B), 4K(D)}	1.942	25.050	1.392	20.59
		{3Fe(B), 1Cr(B), 4K(D)}	1.696	15.340	1.094	16.527
	B	{8Fe(A, C)}	2.452	30.490	2.652	29.805
		{7Fe(A, C), 1Cr(A, C)}	2.351	27.410	2.480	28.565
0.25	(A, C)	{4Fe(B), 4K(D)}	1.955	25.510	1.582	20.630
		{3Fe(B), 1Cr(B), 4K(D)}	1.710	15.902	1.088	15.416
		{2Fe(B), 2Cr(B), 4K(D)}	1.195	13.640	1.036	11.217
	B	{8Fe(A, C)}	2.512	32.640	2.701	29.516
		{7Fe(A, C), 1Cr(A, C)}	2.367	27.630	2.522	28.005
		{6Fe(A, C), 2Cr(A, C)}	2.260	18.820	2.329	27.514
0.375	(A, C)	{4Fe(B), 4K(D)}	1.898	18.680	1.560	16.307
		{3Fe(B), 1Cr(B), 4K(D)}	1.669	15.341	0.876	12.980
		{2Fe(B), 2Cr(B), 4K(D)}	1.147	13.556	0.686	9.298
		{1Fe(B), 3Cr(B), 4K(D)}	0.480	7.673	0.374	5.498
	B	{8Fe(A, C)}	2.563	31.019	2.856	30.373
		{7Fe(A, C), 1Cr(A, C)}	2.377	26.387	2.693	28.396
		{6Fe(A, C), 2Cr(A, C)}	2.259	23.108	2.532	25.772
		{5Fe(A, C), 3Cr(A, C)}	2.23	18.930	2.414	22.685
0.5	(A, C)	{4Fe(B), 4K(D)}	1.994	18.466	1.496	16.529
		{3Fe(B), 1Cr(B), 4K(D)}	1.756	18.746	0.866	13.709
		{2Fe(B), 2Cr(B), 4K(D)}	1.210	14.045	0.662	10.524
		{1Fe(B), 3Cr(B), 4K(D)}	0.473	6.872	0.171	5.432
		{4Cr(B), 4Al(D)}	0.049	3.468	-0.289	1.150
	B	{8Fe(A, C)}	2.658	26.927	2.758	30.579
		{7Fe(A, C), 1Cr(A, C)}	2.389	24.181	2.516	26.761
		{6Fe(A, C), 2Cr(A, C)}	2.329	20.478	2.388	24.044
		{5Fe(A, C), 3Cr(A, C)}	2.254	17.380	2.324	22.057
		{4Fe(A, C), 4Cr(A, C)}	2.196	13.056	2.322	17.686

In Figures 2 and 3 the dependencies of local magnetic moments for Fe(A, C) and Fe(B) on the concentration of chromium for  $Fe_{3-x}Cr_xAl$  and  $Fe_{3-x}Cr_xSi$  are presented.

The local magnetic moments of Fe in (A, C) positions of  $Fe_{3-x}Cr_xAl$  are rather independent of the chromium concentration (Fig. 2 – upper panel) for all considered nearest neighbour environments. The values of the magnetic moment of Fe at B-sites (Fig. 2 – lower panel) slightly grow up with concentration of Cr for most of the local considered environments.

In case of  $Fe_{3-x}Cr_xSi$  the value of magnetic moment of Fe(A, C) increases insignificantly with the concentration only for the first nearest neighbour shell with four Fe and four Si atoms (Fig. 3 – upper panel). For other n.n. shells the magnetic moment of Fe(A, C) decreases with concentration of Cr. The magnetic moment of Fe(B) for all examined nearest neighbour shells (Fig. 3 – lower panel) grows up till  $x = 0.375$  and drops for the highest concentration.

Such behaviour of the local magnetic moment of iron in B position in both of alloys, which is presented here, was observed only after taking the non-local exchange-correlation into account. Without this corrections values of magnetic moments and hyperfine fields are on average 5 percent smaller and rather constant considering the same nearest neighbourhood.

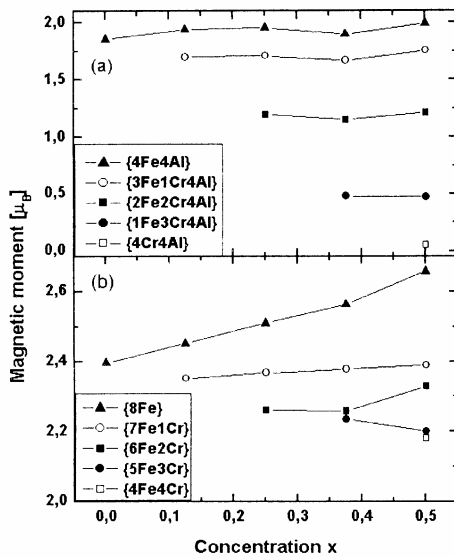


Fig. 2. The local magnetic moment of iron on a) (A, C) and b) B sites for  $Fe_{3-x}Cr_xAl$

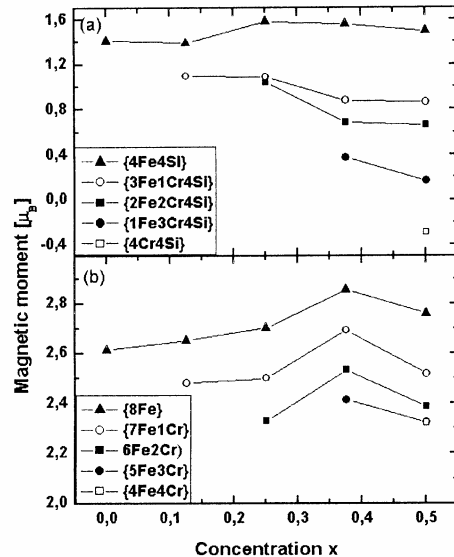


Fig. 3. The local magnetic moment of iron on a) (A, C) and b) B sites for  $Fe_{3-x}Cr_xSi$

The calculated dependence of hyperfine fields for Fe(A, C) and Fe(B) on the concentration of Cr atom is shown in Fig. 4 and 5 for  $Fe_{3-x}Cr_xAl$  and  $Fe_{3-x}Cr_xSi$ , respectively. The substantial decrease of hyperfine field is observed with the decrease of the number of nearest neighbour iron atoms. Every additional Cr atom in the first nearest neighbour shell reduces the hyperfine field, but especially in  $Fe_{3-x}Cr_xAl$  alloys the decrease is not uniform. The similar, although much weaker effect is observed when concentration of Cr increases. Magnetisation of the surrounding atoms induces, *via* hybridisation, the polarisation of valence

4s and 4p electrons having non-vanishing spin density at iron nucleus. The polarised electron density of the nearest neighbour shell also strongly influences the 3d electron spin density of the examined site. The local 3d magnetic moment induces the negative polarisation of the core (1s-3s electrons), which is the dominant source of hyperfine field.

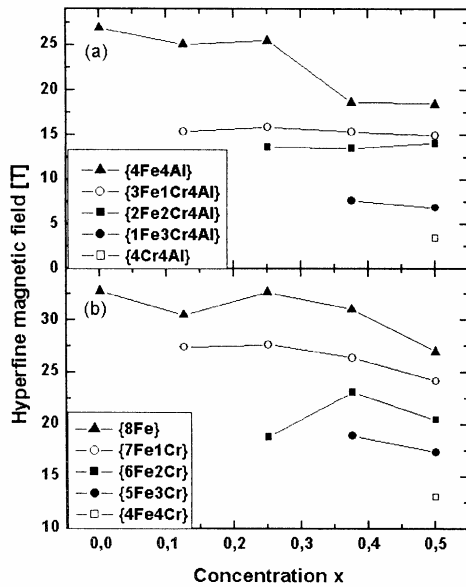


Fig. 4. Hyperfine magnetic fields of iron on a) (A, C) and b) B sites for  $\text{Fe}_{3-x}\text{Cr}_x\text{Al}$

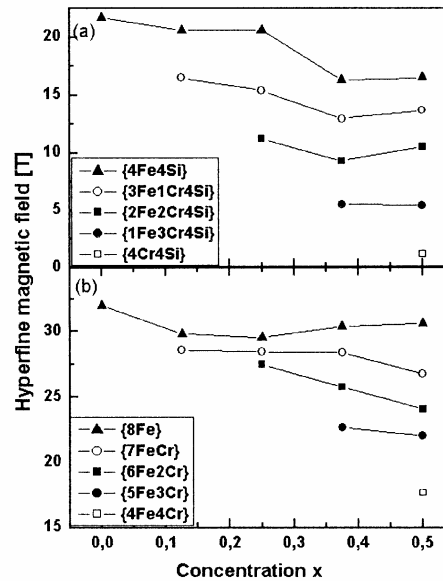


Fig. 5. Hyperfine magnetic fields of iron on a) (A, C) and b) B sites for  $\text{Fe}_{3-x}\text{Cr}_x\text{Si}$

The calculated hyperfine fields are in good agreement with experimental data [1, 2, 7-9]. In  $\text{Fe}_3\text{Al}$  and  $\text{Fe}_3\text{Si}$  the transition metal impurities like chromium perturb the neighbouring iron atoms strongly enough to hybridise the 3d, 4s and 4p atomic orbitals. The influence of short-range order on the local magnetic moment and hyperfine field shows that this perturbation is local and therefore especially efficient when Cr atoms occupies the first neighbouring sites of the iron atoms at both (A, C) and B positions.

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