

Proceedings of the European Conference "Physics of Magnetism 96", Poznań 1996

THEORETICAL AND MÖSSBAUER EFFECT STUDY OF MAGNETIC AND ELECTRONIC PROPERTIES OF Fe_3Al COMPOUND

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The electronic properties of Fe_3Al were determined experimentally, with the use of the Mössbauer spectroscopy, and theoretically. The band structure of the compounds was investigated applying the self-consistent tight-binding linear muffin tin orbital method. The calculated Fermi contact term of hyperfine fields and the isomer shifts are in good agreement with the values resulting from analysis of experimental data. The different kinds of electron transfer estimated on the base of the proposed "additive model" are also strongly supported by calculations.

PACS numbers: 75.50.Bb, 76.80.+y

Iron-aluminium alloys (up to 50 at.% Al) offer excellent opportunities for the study of magnetic properties and electron transfer between constituents as a function of type as well as degree of atomic order. The crystal structures of these alloys are all founded on the bcc lattice. The arrangement in this lattice depends on the composition, thermal and mechanical treatment. Two of these configurations are the ordered B2 structure of FeAl and DO_3 structure of Fe_3Al compounds. Within the unit cell of FeAl compound iron atom is surrounded by eight Al atoms. In DO_3 structure unit cell there are two types of iron atom. The first, denoted by Fe(I), surrounded by eight iron atoms and the other, denoted by Fe(II), surrounded by four aluminium and four iron atoms (see Fig. 1 in Ref. [1]). The experimental lattice constant of FeAl and Fe_3Al is 29.09 nm and 57.92 nm, respectively.

The Mössbauer and free positron lifetime measurements of Fe_3Al suggest that the electron density at Fe(I) atoms is slightly reduced relatively to that of pure α -Fe. The isomer shift values for Fe(I) and Fe(II) are equal to 0.044 mm/s and 0.184 mm/s, respectively [2-4]. On the base of the Mössbauer spectroscopy data a phenomenological model (the so-called additive model) which describes the change of electronic structure of Fe atoms in Fe-Al system was proposed [4]. Two kinds of electron transfer were considered: (i) an intraatomic $4s$ - $3d$ electron conversion, (ii) a transfer of $s(p)$ electrons from neighbouring Al atoms to the $3d$ -band of

Fe atoms. An interatomic electron transfer from Fe(I) to Fe(II) atom was also postulated for explaining the experimental observations. The model relates the isomer shift and the difference in the hyperfine magnetic field ΔB_{hf} relatively to α -Fe with the change in number of 3d (Q_d) and 4s (Q_s) electrons in iron by the formula $\Delta B_{\text{hf}} = A_s Q_s + A_d Q_d$ and $\Delta IS = -2Q_s + 0.2Q_d$, where $A_s = 130.90$ MA/m and $A_d = -6.76$ MA/m are the hyperfine field coupling constants for the 4s and 3d electrons, respectively.

The bcc Fe-Al alloy as well as FeAl and Fe₃Al compounds have been the subject of theoretical investigations with the use of band structure methods [1, 5-7]. Cluster calculations of Elzain and Yousif [7] for Fe-Al bcc alloy reveal existence of electron transfer between constituents. The 3d occupation of iron increases with the rate 0.07 electrons per Al in the nearest neighbour (NN) shell. Some information on the interatomic electronic transfers within the unit cell of FeAl and Fe₃Al compounds can be found in the work of Müller et al. [5] and Ishida et al. [1]. Calculations for FeAl compound have shown that Fe atoms gain electrons at the cost of aluminium [5]. According to results of Ishida et al. for Fe₃Al the aluminium atoms lose some portion of electrons, while the Fe(I) and Fe(II) atoms gain electrons.

It was interesting to calculate electronic structure of FeAl and Fe₃Al compounds once more with an emphasize put on electron transfer within the unit cell. We performed the self-consistent spin-polarized calculations based on the tight binding-linear muffin tin orbitals method in the scalar-relativistic approximation [8]. The method treats the crystal according to the atomic sphere approximation (ASA). The calculated electron transfers are very sensitive to the choice of Wigner-Seitz (W-S) sphere radii. We performed band structure calculations with the use of two sets of radii. For one of them ($r_{\text{WS}}^{\text{Fe}} = 13.83$ nm in FeAl, $r_{\text{WS}}^{\text{Fe(I)}} = 14.05$ nm and $r_{\text{WS}}^{\text{Fe(II)}} = 14.04$ nm in Fe₃Al) the charge neutrality of W-S spheres is preserved. The second set of W-S radii, $r_{\text{WS}}^{\text{Fe}} = 14.91$ nm in FeAl, $r_{\text{WS}}^{\text{Fe(I)}} = 13.62$ nm and $r_{\text{WS}}^{\text{Fe(II)}} = 14.69$ nm in Fe₃Al, is chosen within the so-called "zero step potential approach" (the discontinuity of the effective potential at W-S spheres of the inequivalent atoms within unit cell is removed). In the calculations experimental values of lattice constants were used. For calculations of α -Fe the lattice constant was taken equal to 28.7 nm ($r_{\text{WS}}^{\alpha\text{-Fe}} = 14.13$ nm). The hyperfine field was calculated according to relativistic formula given by Blügel et al. [9] in which the average spin density over the Thomson sphere is taken into account. The isomer shift is calculated with the use of the formula $IS = -0.24\Delta\rho_{4s}(0)$, neglecting the contribution of core electrons (which contribute only in 10% [10]).

The quantitative results of the calculations for α -Fe, FeAl and Fe₃Al are summarized in Tables I and II. Having analysed partial occupation numbers given in Table I the following observations concerning electron transfers can be made. Within the charge neutrality approach (interatomic electron transfer less than 10^{-7} electrons) it is evident that the presence of Al atoms within NN shell of iron forces the intraatomic 4s(*p*)-3d electron conversion. This process leads to the increase in *d*-states occupation number by 0.202 for Fe in FeAl (8 NN Al) and by 0.086 for Fe(II) in Fe₃Al (4 NN Al). For Fe(I) in Fe₃Al, with no nearest

TABLE I

The partial occupation numbers (n_i), local magnetic moment (M) and the total electron transfer (ΔQ) for Fe W-S spheres in pure α -Fe, FeAl and Fe₃Al compounds (negative values of ΔQ indicate the outward electron transfer). Data in brackets (...) represent the results of charge neutrality approach.

	Spin	n_s	n_p	n_d	n_{tot}	M [μ_B]	ΔQ
Fe	\uparrow	0.313	0.364	4.451	5.128	2.26	-
(in α -Fe)	\downarrow	0.328	0.426	2.118	2.872		
Fe	$\uparrow + \downarrow$	0.682	0.942	7.063	8.688	-	+0.688
(in FeAl)		(0.544)	(0.685)	(6.771)	(8.000)	-	(-)
Fe(I)	\uparrow	0.284	0.321	4.463	5.068		
(in Fe ₃ Al)	\downarrow	(0.314)	(0.371)	(4.495)	(5.180)	2.43	-0.295
		0.291	0.360	1.986	2.637	(2.36)	(-)
		(0.322)	(0.417)	(2.082)	(2.821)		
Fe(II)	\uparrow	0.328	0.434	4.357	5.119		
(in Fe ₃ Al)	\downarrow	(0.286)	(0.360)	(4.290)	(4.936)	1.82	+0.413
		0.339	0.488	2.467	3.294	(1.87)	(-)
		(0.295)	(0.403)	(2.366)	(3.064)		

TABLE II

Calculated values of hyperfine field B_{hf} (decomposed into core and valence electron contribution), $4s$ -charge density at iron nucleus $\rho_{4s}(0)$ and the difference of hyperfine field ΔB_{hf} and isomer shift ΔIS relatively to the α -Fe.

	B_{hf} [MA/m]			ΔB_{hf} [MA/m]	$\rho_{4s}(0)$ [a.u. ⁻³]	ΔIS [mm/s]
	core	valence	total			
Fe (in α -Fe)	19.02	4.93	23.95	-	7.916	-
Fe	-	-	-	-	6.932	+0.2362
(in FeAl)					(6.968)	(+0.2275)
Fe(I)	21.65	2.15	23.79	-0.16	7.996	-0.0192
(in Fe ₃ Al)	(21.33)	(2.23)	(23.55)	(-0.40)	(8.069)	(-0.0367)
Fe(II)	16.00	2.86	18.86	-5.09	7.168	+0.1795
(in Fe ₃ Al)	(16.95)	(2.55)	(19.42)	(-4.54)	(7.180)	(+0.1766)

neighbour Al atoms, the intraatomic conversion is negligible. Within the "zero step potential" approach (potential step less than 10^{-5} Ry) the resulted picture of electron transfers is more complicated. Strong interatomic electron transfer is observed between constituents of unit cell. In FeAl compound iron atom gains 0.688 electrons at the cost of $2sp$ electrons of aluminium atom. From these 0.688 electrons 0.494 goes to the $3d$ band of Fe. The number of $4s$ electrons of Fe increases only

slightly (by 0.0417). It means that the intraatomic conversion process ($4sp-3d$) takes place in Fe atom. In Fe_3Al compound we observe the electron interatomic transfer from Al and Fe(I) W-S spheres to the Fe(II) one. Atoms Al and Fe(I) lose 0.531 and 0.295 electrons, respectively. Consequently each of the Fe(II) atoms gains 0.413 electrons. Analysis of changes of partial occupation numbers in Fe(I), Fe(II) and Al W-S spheres showed that the interatomic electron transfer to Fe(II) is associated with the intraatomic $4sp-3d$ conversion process at Fe(II) site. Effectively we found $Q_s = 0.042$, $Q_d = 0.494$ for Fe in FeAl, $Q_s = -0.065$, $Q_d = -0.121$ for Fe(I) and $Q_s = 0.0258$, $Q_d = 0.255$ for Fe(II) in Fe_3Al .

In Table II the calculated values of hyperfine field B_{hf} , the changes of hyperfine field ΔB_{hf} relatively to α -Fe, charge density at Fe nucleus $\rho(0)$ and the isomer shift ΔIS for α -Fe, FeAl and Fe_3Al are given. The calculated values are in good quantitative agreement with the experimental ones. The measured hyperfine field for Fe_3Al is 23.55 MA/m and 16.80 MA/m for Fe(I) and Fe(II), respectively. The changes of isomer shift measured on Fe atom in FeAl compound is equal to 0.28 mm/s [4]. Small negative value of ΔIS obtained for Fe(I) in Fe_3Al differs in sign from the experimental results presented by Frąckowiak [4], although it was reported that the isomer shift observed in Fe-Al alloys on iron surrounded by eight Fe atoms can be small negative (-0.08 mm/s) [11].

The calculations of electron transfer on different type of Fe atoms in FeAl and Fe_3Al compounds are in qualitative agreement with experimental ones. The different kinds of electron transfer proposed in [3, 4] are also strongly supported. It was found that for the calculated values of Q_s and Q_d the enhancement of the d -screening part within the formula of "additive model" for isomer shift yields the results which agree qualitatively with experiment.

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