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Hyperfine Interactions in ZrFe₂ Compounds

INTRODUCTION

Intermetallic compounds have been extensively investigated, mainly because of their specific magnetic behaviour. Apart from the bulk systems also superlattices, interfaces and surface phenomena have been studied. Information about a local environment of nuclear probes may be obtained from measurements of hyperfine interactions.

Quasibinary compounds of ZrFe₂-type belong to the large group of Laves' phase compounds.



Fig. 1. Crystallographic structures of AB₂ compounds

The general formulae of Laves' phase is AB_2 . By the combination between the elements of the A and B atoms, these compounds form three typical crystal structures: cubic MgCu₂ — type (C15) and two kinds of hexagonal structure MgZn₂ — type (C14) and MgNi₂ (C36). All the Fe compounds AFe_2 are ferromagnetic and such compounds are the subject of our investigation. Some of them (e.g. HfFe₂) crystallize in the hexagonal (C14) structure. The others (e.g. ZrFe₂) have the cubic (C15) structure.

Magnetic properties of $ZrFe_2$ compounds are determined by the Fe sublattice. In hexagonal elementary cell the Fe atoms are placed on parallel surfaces (Fig. 1a). In the cubic structure the Fe sublattice may be seen to be constructed from tetrahedra linked by a vertex (Fig. 1b). The line passing through the center of base triangle is taken as the z — direction, the principal axis of the electric field gradient (Fig. 2). The easy magnetization axis lies along < 111 > direction. In this way two possible sites can be distinguished in which the Fe atoms are placed. The population ratio of these sites is equal to 3:1 (I:II). Except for this aspect of non-coincidence of the local z axis and the magnetization direction, the whole geometry is the same for both sites.



Fig. 2. Schematic representation of the Fe sublattice in AB2, C15 structure compounds

The ⁵⁷Fe Mössbauer spectroscopy allows to measure the hyperfine interaction parameters for these crystallographic sites where the Fe atoms are placed. Application of Time Differential Perturbed Angular Correlations method gives the possibility to measure the hyperfine magnetic fields acting on the Ta nuclei placed at the Zr sites. TDPAC measurements have been performed for (133-482) keV cascade in ¹⁸¹Ta (after the β^{-} decay of ¹⁸¹IIf). A standard spectrometer has been used, with BaF₂ and NE111 scintillators working with XP 2020Q photomultiplier. The time resolution was equal to $2\tau_0 = 0.9 - 1.9$ ns. Measurements were performed on polycrystalline samples, without the external magnetic field.

The Mössbauer spectra were recorded at RT with a conventional constant acceleration spectrometer with a ⁵⁷Co source in a Cr matrix.

INTERNAL MAGNETIC FIELDS IN (Zr_xHf_{1-x})Fe₂ COMPOUNDS

The magnetism of metals and compounds is correlated with the crystallographic and electric structure of them. However, it is not exactly known which of these two factors plays a dominant role. The effective tool in the studies of magnetic properties and stability of crystallographic structure are measurements of hyperfine fields in the substitutional, quasibinary compounds as a function of the concentration of admixtured atoms. Our measurements confirmed the supposition that the substitution of magnetic atoms (Fe) and nonmagnetic (Zr) ones led to the different results.



Fig. 3. Hyperfine magnetic field on Ta nuclei in $(Zr_xHf_{1-x})Fe_2$ as a function of the Zr concentrations

In the beginning, the changes of hyperfine interaction parameters caused by the substitution of the Zr atoms by the Hf atoms were measured. In Fig. 3 the changes of hyperfine magnetic field B_{hf} acting on Ta nuclei in $(Zr_xHf_{1-x})Fe_2$ compounds are presented.

In spite of the fact that zirconium and hafnium belong to the different periods in the periodic table of elements, their chemical properties are very similar. It is visible in Fig. 3 that the substitution of the Zr atoms by the Hf atoms does not change the hyperfine magnetic field on Ta nuclei $(B_{\rm hf}^1)$ in the wide range of concentration $0.4 \le x \le 1.0$. Not before $x \le 0.3$, the component $B_{\rm hf}^2$ characteristic of HfFe₂ appears. For lower concentration x we have observed the additional component $B_{\rm hf}^3$ attributed by us to the crystallographic unstability of HfFe₂.

The substitution of zirconium by the Hf atoms for the whole range of concentration x does not influence the hyperfine magnetic field on ⁵⁷Fe nuclei (at B sites) [1].



Fig. 4. Reduced values of hyperfine magnetic fields on ¹⁸¹Ta and ⁵⁷Fe nuclei as the functions of the reduced temperature. Solid lines stand the Brillouin functions for J = 1/2 and J = 7/2

For considerable amount of zirconium $(x \ge 0.4)$, the anomalous behaviour of hyperfine magnetic fields on ¹⁸¹Ta as well as on ⁵⁷Fe nuclei was observed, Fig. 4. Such a behaviour was attributed [2] to the contribution from the core polarization of the Ta atoms, caused by the localized magnetic moment of the iron.

INFLUENCE OF THE NEAREST SURROUNDING OF
57
Fe IN $Zr(Fe_{1-x}Al_x)_2$
AND $Zr(Fe_{1-x}Si_x)_2$ COMPOUNDS

A partial replacement of the Fe atoms by nonmagnetic Al and Si was an attempt to determine the influence of such a substitution on the hyperfine interaction parameters.

In order to attain this information we have used Mössbauer spectroscopy. Mössbauer spectra were recorded with a conventional constant acceleration spectrometer with a ⁵⁷Co source in a Cr matrix.



The substitution of the Fe atoms by Al and Si causes a great variety of 57 Fe local environments, under the assumption that the admixtured atoms are distributed randomly. In Fig. 5 the mean weighted values of hyperfine magnetic field (B), isomer shift (IS) and quadrupole splitting (QS) are shown as the functions of Al and Si concentration. It reveals, that aluminium and silicon being neigbours in the periodic table of elements cause the similar changes of the hyperfine interaction parameters. It is visible particularly in the case of hyperfine magnetic field. The range of interest (0.00 $\leq x \leq 0.20$) may be divided into two parts showing different

 $\operatorname{Zr}(\operatorname{Fe}_{1-x}\operatorname{Si}_x)_2$.

As it was mentioned above (see also Fig. 2), in pure $ZrFe_2$ the Fe atoms may occupy two, magnetically inequivalent sites. It stands to reason that our Mössbauer spectra registered for x = 0 consist of two sextuplets. The total intensity ratio is closed to the expected one 3:1. All the spectra for x > 0 have been fitted by more than two sextuplets. The total intensity and QS ratio differ significantly from 3 : 1 and -1 : 3, respectively. It means, in our opinion, that the direction of the easy magnetization axis has changed from [111] to [100], at least locally.

slopes of curves. For $x \cong 0.06$, the inflection occurs for $Zr(Fe_{1-x}Al_x)_2$ as well as for

More than two sextuplets in our spectra for higher concentration of Al or Si result from a great variety of the Fe local environments. In pure ZrFe₂ the iron atom



Fig. 6. Components of hyperfine magnetic fields in $Zr(Fe_{1-x}Al_x)_2$ (upper figure) and $Zr(Fe_{1-x}Sl_x)_2$ (lower figure) as the function of Al and Si concentration, respectively

is surrounded by 6 Fe atoms as its nearest neighbours (nn) and 12 Fe atoms as the next-nearest neighbours (nnn). With growing concentration of admixtured atoms (Al, Si) more and more of them become nearest and next-nearest neighbours of the Fe atom. Fig. 6 presents the behaviour of all components of hyperfine magnetic fields with growing concentration of nonmagnetic atoms (Al, Si).

It is visible that the character of changes is very similar for both our compounds. Such a dependence allows us to attribute a given number of nonmagnetic atoms to every individual component assuming that each of them reflects a probable local environment of the Fe atom. The proposed configurations of Fe and Al and Si atoms are presented in Table 1. Under the supposition of such a configuration as given in the Table 1, the divergence between experimental and theoretical amplitude values remains within the bounds of $10 \div 30\%$ for $x \le 0.10$ and $30 \div 50\%$ for $x \ge 0.13$. The configurations presented for e) and f) curves are very rough estimations. The bifurcation of curves a) for $x \le 0.06$ results from the existence of two possible, magnetically inequivalent Fe sites in Z_1Fe_2 . With increasing Al(Si) concentration, this splitting disappears. Under the assumption of a random distribution of admixtured atoms, the probability of finding a definite surrounding of the Fe atom may be calculated from the binomial distribution.

Curve	Configuration of						
in	nn shell	nnn shell					
Fig. 3		$X \leq 0.10$	$x \ge 0.13$				
a	6Fe	12Fe	12Fe, <u>11Fe+1Si</u>				
b	6Fe	11Fe+1Si	<u>11Fe+1Si</u> , 10Fe+2Si				
с	5Fe+1Si	<u>12Fe</u>	11Fe+1Si, 10Fe+2Si				
	6Fe	10Fe+2Si	10Fe+2Si, 9Fe+3Si				
d	5Fe+1Si	11Fe+1Si, 10Fe+2Si	11Fe+1Si, 10Fe+2Si				
	6Fe	9Fe+3Si	9Fe+3Si, 9Fe+3Si				
e	4Fe+2Si	12Fe, 11Fe+1Si	12Fe, 11Fe+1Si				
			10Fe+2Si				
1	4Fe+2Si	10Fe+2Si, 9Fe+3Si	10Fe+2Si, 9Fe+3Si				
			8Fe+4Si				

Table 1. The proposed configurations of Fe and Al(Si) atoms in the nearest (nn) and next--nearest (nnn) shells of ⁵⁷Fe atoms, corresponding to curves (a-f) of Fig. 6. The underlined configurations provide the largest contribution to the amplitude of hyperfine magnetic field

A confrontation of experimental amplitudes of sextuplets (a-f) obtained from numerical analysis and binominal distribution data shows a divergence between them within the bounds of 30%. It is the satisfactory agreement considering that only the arrangements of frequent occurrence are detected. Furthermore, one should remember that between the atoms of admixture (Al, Si) introduced into metallic compound the repulsion or the attraction may occur. Such the interaction have been studied in metals [3].

Our results indicate that the decreasing of hyperfine magnetic fields at the Fe sites (and thereby the decrease of the Fe magnetic moment) is caused by increasing number of nonmagnetic atoms (Al, Si) in the nearest surrounding of the Fe atom. It becomes evident, from our studies, that the concentration dependence of the hyperfine magnetic field cannot be explained by assuming a discontinues formation of the Fe magnetic moment on the basis of the model of Jaccarino and Walker[4]. According to this model the magnetic moment of the Fe atom should be equal to zero or should have its maximum value depending on the number of magnetic neigbours. It reveals from our experiment, that the decrease of the Fe magnetic moment is rather stepwise. We have estimated from our spectra that the lack of one Fe atom as the nearest neigbour causes the decrease of the field by about 34 kGs. The substitution of one Fe atom as the next-nearest neighbour causes the decrease by about 8 kGs.

LOCALIZATION OF MAGNETIC MOMENT

There are two theoretical approaches which may be applied to the description of properties of magnetic materials. Heisenberg set fourth a theory which assumed that the carriers of magnetic moments were localized and their energetic spectrum was described by Boltzman statistics [5].

The second approach assumes that the magnetic electrons are itinerant and they are described, in S t o n er's opinion [6], by Fermi — Dirac statistics. The energetic structure of the magnetic material should be the determination in the acceptation of the adequate theoretical approach. If the width of the electronic levels in a crystal is considerably smaller than the energy difference between them this crystal should be described by the Heisenberg's model of localized moments. Whereas the energy difference between electronic levels is comparable with their width, the magnetic properties may be described by the band model (itinerant electrons). In this aspect one should remember that in our compounds we have two crystallographic sites where the Fe atoms and Zr(Hf) atoms are located.

It results from our Mössbauer measurements that the localized magnetic moments in the Fe sites decreases with growing amount of nonmagnetic atoms in its nearest surrounding. Regarding the Zr(Hf) sites, the information was given by TD-PAC data. From the lack of anomaly in the temperature dependence of hyperfine magnetic field on ¹⁸¹Ta nuclei (Fig. 4) results that in the IIf sites the localized magnetic moment rather does not exist. The measured value $B_{hf}(Ta) = -146(3)$ kGs originates mainly from the polarization of the conduction electrons. This polarization is proportional to the magnetization of the iron sublattice and exhibits the same temperature dependence. The temperature anomaly appears for $x \ge 0.4$. We may admit that then the localized magnetic moment at Zr, IIf(Ta) sites appears in (Zr_{0.4}Hf_{0.6})Fe₂ and it is approximately constant up to the total substitution of the Hf by the Zr atoms.

In $ZrFe_2$ the macroscopic magnetic moment per one Fe atom is equal to 1.60 μ_B [7] and it is by about 20% greater than in the case of HfFe₂ (1.30 μ_B [8]). It means that the contribution from the polarization of conduction electrons increases to about -170 kGs. Thus, the contribution from the core polarization can be estimated as equal to about +100 kGs (at room temperature). It means that at Zr sites the magnetic moment with opposite sign appears. It is induced by the Fe sublattice.

sample	nuclear	Bhf (kGs)	∂ln B _{hf} /∂p	T	Ref.
	probe	at p=0	$(10^{-12} \text{ Pa}^{-1})$		
$(Zr_{0.9}Hf_{0.1})Fe_2$	^{IRI} Ta	-65(10)	22.3(3)	RT	9
ZrFe ₂	⁸⁹ Zr	-126(10)	11.1(3)	L He	10
ZrFe2	⁵⁷ Fe	-222(10)	-7.3(1)	LHe	10

Table 2. Hyperfine magnetic fields and their pressure derivatives in the compounds of ZrFe2 type

The confirmation of this fact was given by measurements of pressure derivatives of hyperfine magnetic field in $(Zr_{0.9}Hf_{0.1})_2$ [8]. Table 2 presents the results of our measurements and the data from other works.

It is visible that the pressure derivatives of B_{hf} at the Zr sites (occupied also by Hf(Ta)) have the sign opposite to that one at the Fe sites. These results confirmed the theoretical predictions set forth by two independent groups: $\mu_{Zr} = -0.53\mu_B$, $\mu_{Fe} = 1.87\mu_B$, [11] and $\mu_{Zr} = -0.56\mu_B$, $\mu_{Fe} = 1.90\mu_B$ [12].

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