

J. SARZYŃSKI, M. BUDZYŃSKI, R. WASIEWICZ, H. SPUSTEK,
W. TAŃSKA-KRUPA

TDPAC and Mössbauer Measurements in $Y(Fe_{1-x}Al_x)_2$ and $Zr(Fe_{1-x}Al_x)_2$
Laves Phase Compounds for $x \leq 0.20$

ABSTRACT

Hyperfine interactions have been investigated in the system $R(Fe_{1-x}Al_x)_2$, ($R=Y, Zr$) as a function of Al concentration, x . The ^{57}Fe Mössbauer effect and ^{181}Ta TDPAC measurements have been performed at RT, in the concentration range from $x=0.00$ to $x=0.20$. It was found that the hyperfine magnetic field is notably reduced by change of local atomic ordering.

1. INTRODUCTION.

The pseudobinary systems $Y(Fe_{1-x}Al_x)_2$ and $Zr(Fe_{1-x}Al_x)_2$ have been extensively studied, mainly because of their specific magnetic behaviour. In spite of the bulk magnetization

measurements, also the hyperfine interaction studies provide important contribution to the discussion of the magnetic properties of these systems. There exist two models explaining the magnetic properties of these compounds, i.e. the Jaccarino-Walker model [1] and the second one described by Van der Kraan et al. [2]. Uncomplete and sometimes contradictory experimental data are not able to determine the range of application of these models. We try to contribute to this discussion experimentally.

2. EXPERIMENTAL PROCEDURE.

The $Y(Fe_{1-x}Al_x)_2$ and $Zr(Fe_{1-x}Al_x)_2$ compounds were prepared by arc melting in an argon atmosphere. The annealing of samples in vacuum $\cong 10^{-4}$ Pa at temperature 850-900 K for 72 hours has been carried out to increase or to recover their homogeneity and to improve crystalline structure of the material.

It is known that for $Y(Fe_{1-x}Al_x)_2$ and $Zr(Fe_{1-x}Al_x)_2$ the cubic Laves phase is not preserved for all values of x , but that in a certain range a hexagonal structure becomes more stable. Therefore we have limited our study to the range from $x=0.00$ up to $x=0.20$ in which the cubic phase is preserved. The X-ray powder patterns were observed in all samples confirming the phase homogeneity.

The Mössbauer spectra were recorded with a conventional constant acceleration spectrometer with a ^{57}Co source in a Cr matrix.

The samples for TDPAC measurements have been prepared separately. They contained a small fraction (2 atomic % relative to Zr) of ^{180}Hf atoms. We assume that Hf atoms are located in the Y(Zr) sites. These samples have been exposed for 100 h. to the neutron flux $\phi=7 \cdot 10^{13}$ neutrons/cm²s and after that they were annealed to remove the radiation defects. TDPAC measurements have been performed for (133-482) keV γ -ray cascade in ^{181}Ta . A standard correlation spectrometer has been used, with BaF_2 scintillators connected with XP 2020Q photomultipliers. The time resolution was equal to $2\tau_0=0.7$ ns.

All measurements have been performed at room temperature. For the additional measurements of magnetization a special set of samples has been prepared containing 3 atomic % of Hf relative to Zr.

3. RESULTS AND DISCUSSION.

From the Mössbauer spectra, presented in fig. 1 (a,b), the following general conclusion can be derived: the shape of the spectra strongly depends on the Al-content. Starting with $x=0.05$ the spectra become broadened. Therefore they were analysed using a computer program based on the method developed by Window [3]. The obtained results are shown in Tables 1 and 2. The IS scale is given relative to Cr matrix.

In the case of YFe_2 and $ZrFe_2$ the spectra consist of two six-line patterns with intensity ratio 3:1, and the ratio of the quadrupole splitting -1:3, according to the presence of the easy magnetization axis along [111]. For the samples with Al contents, these values are not observed. This can indicate that the axis of easy magnetization has changed to [100], at least locally. Such change of direction has been also observed by NMR investigations of $Y(Fe_{0.99}Al_{0.01})_2$ [4].

A discrete distribution of hyperfine fields for $x>0$, showed in Tables 1 and 2 represents the first approximation only. There are given these hyperfine components with the strongest intensity, for which the best approximation was observed. For the higher concentration of Al, rather continuous distribution of the hyperfine interaction parameters: H, IS and QS can be expected. In the range under investigation, the concentration dependence of the weighted average values of H, IS and QS is roughly the linear. Such dependence has been just shown by earlier works [5,6].

In spite of the precise analysis of our spectra, neither the relation of $H_2:H_1 \cong 5:6$, noticed by H.J. Besnus et al. [7], nor the correlation between IS and QS with the change of Al contents, shown by L. Amaral et al. [8] were observed in our experiment.

With the increase of Al concentration the hyperfine fields on ^{57}Fe nuclei located in different magnetic sublattices come to be smaller. These changes are probably connected, at least partially, with dipol-dipol interaction between nuclear probes and neighbouring atoms. The dipolar contributions are changing with the change of x value. This fact can be predicted by means of P.T.Callagen's et al. [9] procedure.

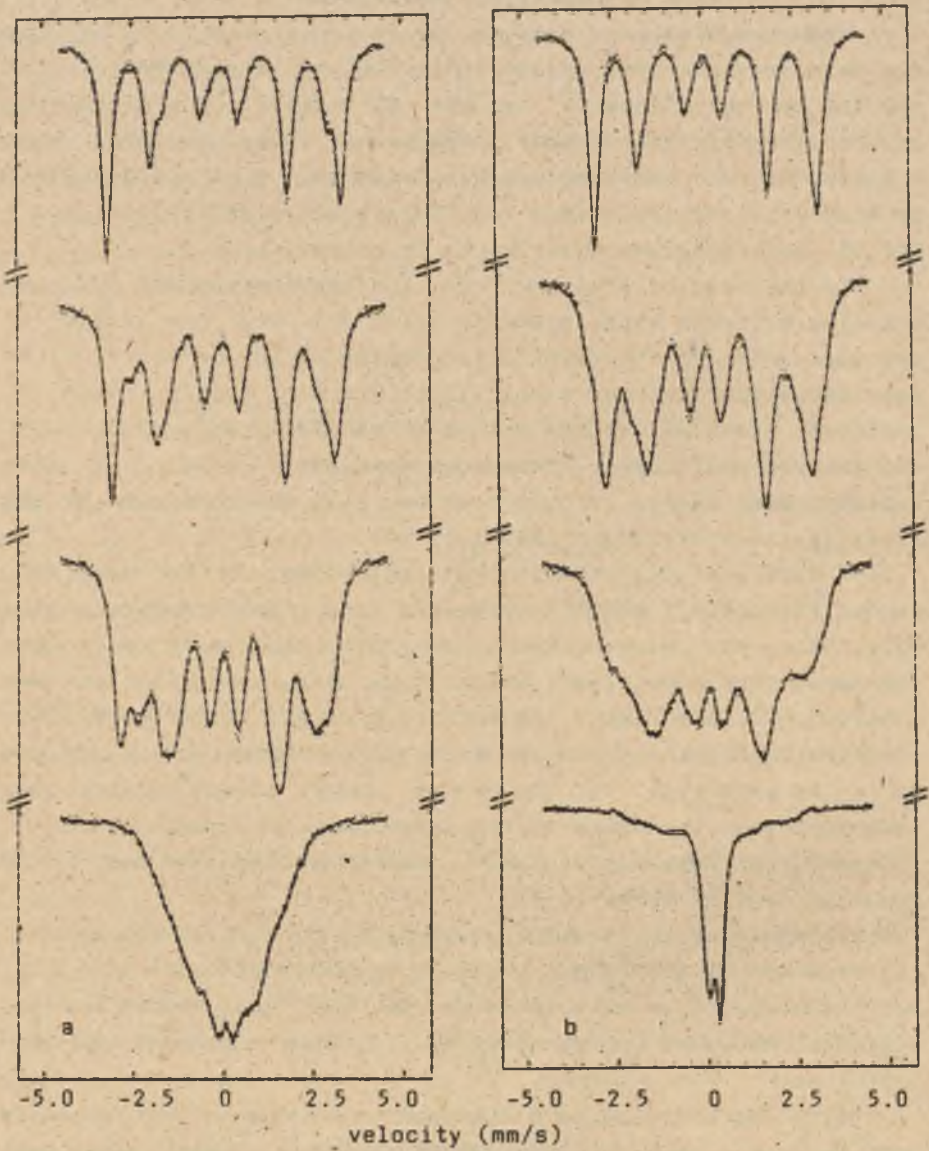


Fig.1. The Mössbauer spectra for $Zr(Fe_{1-x}Al_x)_2$ (a) and $Y(Fe_{1-x}Al_x)_2$ (b) Laves phase compounds. The Al concentrations in these spectra (a,b) are as follows (from top to bottom) $x=0.00$, $x=0.05$, $x=0.10$ and $x=0.20$.

Table 1. Results of the measurements of Mössbauer spectra in $Y(Fe_{1-x}Al_x)_2$ Laves phase compounds.

x	AMPLITUDE (%)	ISOMER SHIFT (mm/s)	HYPERFINE MAGNETIC FIELD (kGs)	QUADRUPOLE SPLITTING (mm/s)
0.00	75.0	0.0748(6)	190.64(5)	-0.0551(5)
	25.0	0.0841(17)	185.96(13)	0.1653(15)
0.05	9.0	-0.0703(48)	206.34(43)	-0.1346(51)
	6.5	0.0827(61)	185.56(58)	-0.1931(82)
	47.4	0.0666(17)	180.52(26)	-0.0140(35)
	15.0	-0.0190(44)	158.12(58)	0.0106(40)
	14.1	0.3071(53)	148.25(45)	-0.0834(47)
	8.0	-0.0494(97)	142.86(86)	0.0387(64)
0.10	10.4	0.0637(59)	183.87(54)	-0.2445(58)
	15.9	0.1210(72)	167.87(75)	-0.1761(73)
	19.7	-0.0910(65)	153.42(54)	0.3140(82)
	20.1	0.2024(58)	138.98(91)	-0.2880(63)
	20.0	0.1511(69)	106.75(68)	0.5638(60)
	13.9	0.1644(93)	106.69(96)	-0.5695(76)
0.20	54.8	0.1048(34)		0.1728(11)
	40.5	0.1952(26)		0.1369(23)
	1.2	0.072(18)	140.1(16)	-0.013(16)
	2.5	0.099(22)	113.1(14)	-0.082(23)
	1.0	0.264(41)	67.1(14)	0.102(22)

Table 2. Results of the measurements of Mössbauer spectra in $Zr(Fe_{1-x}Al_x)_2$ Laves phase compounds.

X	AMPLITUDE (%)	ISOMER SHIFT (mm/s)	HYPERFINE MAGNETIC FIELD (kGs)	QUADRUPOLE SPLITTING (mm/s)
0.00	75.0	-0.0115(7)	202.31(7)	-0.0589(7)
	25.0	0.0088(21)	187.86(22)	0.1767(21)
0.05	32.5	-0.0250(23)	195.54(32)	-0.1019(110)
	24.0	-0.0184(28)	193.65(44)	0.0270(90)
	22.7	0.0022(44)	181.71(83)	0.0703(70)
	16.9	0.0056(56)	158.55(47)	-0.0247(51)
	3.9	0.6189(107)	147.79(82)	-0.3699(107)
0.10	21.5	0.0580(47)	181.79(47)	-0.0457(30)
	21.0	-0.2700(44)	142.38(19)	0.4090(43)
	15.9	0.0232(46)	155.03(64)	-0.0658(51)
	7.2	0.2809(165)	156.22(146)	0.3678(136)
	17.0	0.2248(135)	141.73(55)	-0.2969(122)
0.20	17.4	0.0068(139)	138.22(104)	-0.0491(147)
	7.7	-0.416(14)	128.2(14)	-0.531(12)
	12.8	-0.297(13)	105.9(11)	-0.422(20)
	12.3	0.288(16)	59.1(12)	0.098(14)
	36.4	-0.225(34)	60.8(9)	-0.024(11)
	30.7	0.520(24)	55.3(9)	-0.086(16)

The calculations made by G. Wiesinger et al. [10] have shown that the change of the direction of an easy magnetization axis in $ZrFe_2$ give the dipolar contribution equal to 5 kGs. This is, may be by accident, in accordance with the value obtained in the present work. One should remember that in these calculations, the induction of magnetic moment in the Fe sites was not taken into account, although its existence seems to be confirmed at present.

The additional measurements of magnetization $\sigma(T)$ for $(Zr_{0.97}Hf_{0.03})(Fe_{1-x}Al_x)_2$, from LN temperature to RT have been performed. The obtained results are the same as these known for $Zr(Fe_{1-x}Al_x)_2$. It means that the replacing of no more than 3% Zr atoms by Hf atoms doesn't change the magnetic integral characteristics of our compounds.

Except of the $Y(Fe_{0.8}Al_{0.2})_2$ sample no paramagnetic doublet has been observed in our Mössbauer spectra. This is the indication that none of the Fe atoms has a magnetic moment equal to zero. Thus, the model of Jaccarino and Walker [1] succesfully applied to the explanation of the concentration dependence of the magnetization and of the high χ_{1+1} susceptibility is rather useless in the case of the hyperfine-field investigation. It is well known, that the Zr and Y atoms have no their own magnetic moment. In their sites, however, the magnetic moment exists. It is induced by Fe atoms. This explains the deviation from the Jaccarino-Walker model.

As far as the $Y(Fe_{0.8}Al_{0.2})_2$ sample is concerned the Table 1 and fig.1b show that the contribution of magnetic hyperfine interaction is small and equal to about 5%. It is unquestionable that at temperatures much lower than RT the magnetic interaction would be stronger.

The presence of several six-line patterns is, in our opinion in agreement with the local environment model. The substitution of Fe atoms by Al atoms caused a great variety of local environment. The importance of local environment effects for magnetic properties of the pseudobinary systems, pointed out by M. J. Besnus et al. [7] for the $Y(Fe_{1-x}Al_x)_2$, is rather unquestionable. It has been noticed [11] that for the iron rich concentration ($0 \leq x \leq 0.10$) in $Zr(Fe_{1-x}Al_x)_2$ the spectra could be sufficiently explained by taking into account the nearest neighbour influence only. Present results indicate, that even

for the expanded range of concentration the first-neighbour shell influence is the most important.

The TDPAC spectra are shown in fig. 2. In the Table 3 the results of fitting procedure are presented. The existence of two, precisely determined magnetic fields, acting on Ta nuclei should be taken into the account. We consider that Zr atoms are located only in these sites in crystal lattice which are magnetically equivalent. For $ZrFe_2$ the ratio of ionic radius is equal to the ideal value 1.225. There are no free spaces in the lattice, dimension of which could be comparable with Hf(Ta) atoms dimension. The volume filler was equal to 71 %. As it results from values of their ionic radii, the Hf atoms should occupy the Zr sites. In the samples without Al contents, about 6 % of nuclear probes occupy the sites where there are no magnetic dipole and quadrupole perturbation.

The frequencies of precession curves for the samples containing the Al concentration equal to $x = 0.05$; 0.10 and 0.20 has a large value of the half width. It means that Ta nuclear probes are located in not precisely determined position in the deformed crystal lattice. It seems, that a part of Hf(Ta) atoms is placed in Fe or Al sites. In this situation the lattice deformation results from dissimilarity of ionic radii of these elements.

It is known at present that the magnetic moment at Y, Zr(Ta) sites is induced by Fe atoms. The sign of this moment is opposite to this one at Fe site. Furthermore, the character of spin density oscillations of polarized conduction electrons caused by long-range interactions of RKKY type is periodic. Thus, one can suppose that if the crystal lattice is locally deformed by Ta ions then the comparable contributions from polarization of conduction electrons and from core polarization will be compensative. This may explain the fact that the quantity of nuclear probes which do not undergo the influence of internal magnetic fields is relatively large (7.7(1.5)% for $x=0$).

In the sample with $x=0$ (pure $Zr(Fe)_2$) two magnetic fields $B_1 \cong 60$ kGs and $B_2 \cong 87$ kGs exist. Values of these two fields decrease with an increase of x but in nonmonotonic way. For $x=0.05$ the fields concerned are the smallest ones.

The peculiarity of hyperfine interaction parameters behaviour for $x=0.05$ has been also noticed in ME measurements. This may be connected with a change of the direction of an easy magnetization axis, which takes place in this range of concentration. The comparison between internal fields acting on Fe and Ta nuclei (Tables 2 and 3) in the compounds of $ZrFe_x$ type shows that changes of magnetic fields at Ta sites are more regular. However, one can conclude from literature and measurements performed that situation should be quite different. Fe ions exist in their natural environment in crystal lattice, meanwhile, the neighbourhood of Ta ions is deformed. For the explanation, the additional ME and TDPAC measurements for the samples in the range from $x=0.00$ to $x=0.05$ should be performed.

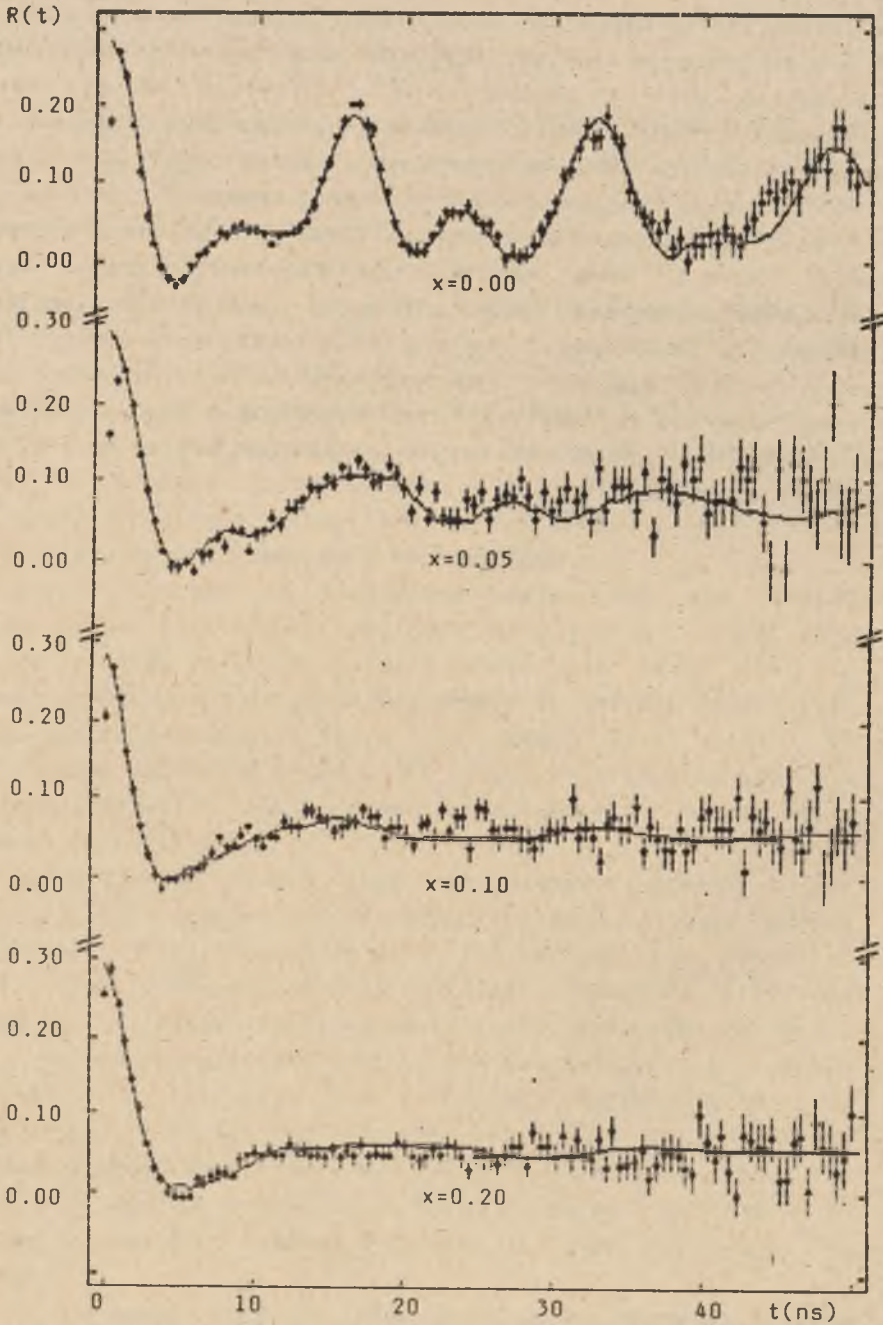


Fig.2. The precession curves $R(t)$ for $Zr(Fe_{1-x}Al_x)_2$ Laves phase compounds for given x values.

Table 3. Results of the TDPAC measurements for ^{181}Ta in $\text{Zr}(\text{Fe}_{1-x}\text{Al}_x)_2$. B and δB represents the mean value of hyperfine magnetic field and FWHM of his distribution, respectively.

x	AMPLITUDE [%]	HYPERFINE MAGNETIC FIELD	
		B [kGs]	δB [kGs]
	67.4(0.9)	60.5(1.1)	1.4(0.1)
0.00	24.9(1.1)	87.1(1.6)	3.5(0.5)
	7.7(1.5)	0.	0.
	57.4(5.3)	54.5(1.1)	6.0(0.7)
0.05	33.8(5.6)	72.7(1.7)	6.2(1.5)
	8.8(7.7)	0.	0.
	38.8(19.3)	59.6(2.1)	10.1(3.0)
0.10	61.2(20.9)	82.7(5.3)	21.8(3.8)
	0.0(28.5)	0.	0.
	65.9(13.4)	51.7(2.2)	15.6(1.4)
0.20	34.1(14.2)	80.6(3.7)	15.4(5.0)
	0.0(19.5)	0.	0.

ACKNOWLEDGEMENTS

The authors acknowledgement the financial support from the Government's Central Program of Fundamental Research CPBP-01.09 in the realization of the present paper.

REFERENCES

1. V. Jaccarino and L.R. Walker. *Phys.Rev.Lett.* 15, 258 (1965).
2. A.M.Van der Kraan, P.C.M. Gubbens and K.H.J. Buschow, *Proc.Int.Conf.Mössbauer Effect*, Bucharest 1977, 121.
3. B. Window, *J.Phys.E:Sci.Instrum.* 4, 401 (1971).
4. A. Oppelt and K.H.J. Buschow, *Phys.Rev.B*, 13, 4698 (1976).
5. G. Wiesinger, *J.Magn.Magn.Mat.* 25, 152 (1981).
6. M. Reissner and W. Steiner, *Hyp.Int.* 28, 1017 (1986).
7. M.J. Besnus, P. Bauer and J.M.Genin, *J.Phys.F:Metal Phys.* 8, 191 (1978).
8. L. Amaral, F.P. Livi and A.A. Gomes, *J.Phys.F:Metal Phys.* 12, 2091 (1982).
9. P.T. Callaghan, P.D. Johnstone and N.J.Stone, *J.Phys.C.Solid State Phys.* 7, 3161 (1974).
10. G. Wiesinger, A. Oppelt and K.H.J. Buschow, *J.Magn.Magn.Mat.* 22, 227 (1981).
11. R. Grössinger, G. Hilscher and G. Wiesinger, *J.Magn.Magn.Mat.* 23, 47 (1981).