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MOSSBAUER ISOMER-SHIFTS AND QUADRUPOLE SPLITTINGS IN THE AMORPHOUS IRON-BORON SYSTEM

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The isomer shifts and quadrupole splittings of amorphous Fe_xB_{1-x} alloys (10 a/o $\lesssim$ x $\lesssim$ 90 a/o) were studied by ^{57}Fe Mössbauer spectroscopy. The isomer shift vs. composition can be described by the $\Delta\phi^*$- and Δn_{WS}-terms of Miedema's cellular model to predict the heat of formation of binary alloys and an additional volume mismatch term. This term is necessary for boron-rich alloys (x $\lesssim$ 50 a/o). We conclude that these samples have a strained atomic structure. The values of the quadrupole splittings at the boron-rich side increase strongly, indicating that the Fe-atoms are squeezed into asymmetric atomic surroundings. Implanted iron into crystalline boron has a comparable isomer shift and quadrupole splitting as the boron-rich alloys.

1. INTRODUCTION

Amorphous Fe_xB_{1-x}-alloys can be prepared by several experimental techniques. Melt quenching with an effective cooling rate of 10^6 K/s is limited to compositions near the deep eutectic at 17 a/o B in the Fe-B phase diagram (72 a/o < x < 88 a/o[1]). Vapour quenching techniques offer a much wider composition range extending from 10 a/o to 90 a/o B, due to the much higher cooling rate of about 10^{16} K/s. Another technique to make amorphous Fe_xB_{1-x} could be implantation of Fe-atoms into boron[2] where the cooling rate is 10^{14} K/s.

^{57}Fe Mössbauer Effect Spectroscopy (MES) provides information about the electronic and magnetic structure of these alloys. In this paper we concentrate on the isomer shift and quadrupole splitting. The isomer shift reflects the charge on the iron atoms, whereas the quadrupole splitting is determined by the charge distribution on neighbouring atoms.

2. EXPERIMENTAL

2.1. Sample preparation

Amorphous Fe_xB_{1-x} samples have been prepared by sputtering on boron nitride substrates kept at room temperature (RT) or liquid nitrogen temperature. Targets of the appropriate compositions were DC-sputtered in an argon-gas atmosphere of 0.1-0.5 Torr (V = 1.5 kV, I = 2mA). Base pressure before sputtering was below 2×10^{-6} Torr. A presputtering cycle of about 30 minutes with a molybdenum

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shutter between the sputter target and the substrate was performed in order to stabilize the sputtering conditions and to activate the gettersputtering-action[3,4], resulting in a very low partial pressure (10^{-10} Torr of lower[4]) of contaminating gases near the substrate. The thickness of the sputtered samples was a few micrometers.

Amorphous iron-boron films on quartz and aluminium substrates were prepared by two-source coevaporation of the elements[13,14]. The base pressure of the vacuum system was about 5×10^{-8} Torr. The thickness of the samples was about 5000 Å. After deposition the thin films were examined by X-ray diffraction (CuK_α) confirming non-crystallinity. Accuracy of composition of the evaporated samples is better than 2 a/o. Until now the composition of the sputtered samples is not known exactly, we assumed that these are equal to the target compositions.

2.2. Mössbauer measurements

Transmission Mössbauer effect spectra of the sputtered samples were recorded in situ. In this work we report only RT measurements. Evaporated samples were measured with MES and CEMS (Conversion Electron Mössbauer Spectroscopy) at RT.

3. RESULTS AND DISCUSSION

3.1. $\overline{IS}$ and $\overline{\Delta E_Q}$ from Mössbauer effect measurements

Amorphous Fe_xB_{1-x} with $x \lesssim 50$ a/o showed paramagnetic spectra[5]. These were fitted by two Lorentzian lines. The mean isomershift $\overline{IS}$ relative to α-Fe and quadrupole splitting $\overline{\Delta E_Q}$ were determined from the peak positions. The ferromagnetic spectra were fitted by a sextuplet of Lorentzians from which only the mean isomer shift is taken in this study. Values of $\overline{IS}$ and $\overline{\Delta E_Q}$ are shown in figures 1 and 2, respectively. The value of $\overline{\Delta E_Q}$ of amorphous $Fe_{82.5}B_{17.5}$ was obtained from the paramagnetic state. This measurement had to be performed very quickly and carefully to avoid crystallization[1]. $\overline{\Delta E_Q}$ was 0.43 mm/sec at 610 K. The corresponding value at room temperature was extrapolated from temperature dependent ΔE_Q measurements to be about 0.52 mm/sec. Values of $\overline{IS}$ and $\overline{\Delta E_Q}$ for ^{57}Fe implanted into crystalline boron[2] are also indicated in figure 1 and 2.

3.2. Interpretation of $\overline{IS}$ with Miedema-Van der Woude model

The Miedema model was originally developed as an empirical model to predict the heat of formation of binary alloys[6]. It was shown by Miedema and Van der Woude[7,8] that the ^{197}Au isomer shift in Au alloys and compounds could also be analyzed in terms of the so-called Miedema parameters and an additional volume mismatch term. According to this Miedema-Van der Woude model the isomer-shift (relative to α-Fe) IS(x) of amorphous Fe_xA_{1-x} alloys is given by:

$$IS(x) = C_s(x)\ \delta(IS)_{max} \cdot \qquad (1)$$

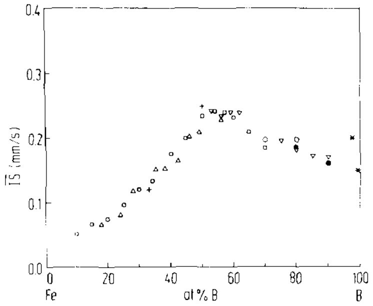

FIGURE 1

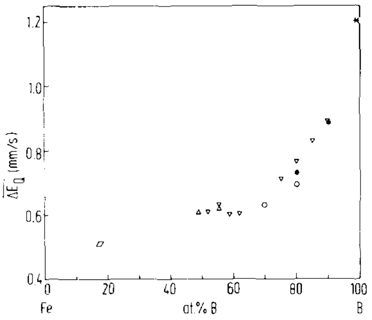

FIGURE 2

Mean isomer shift $\overline{IS}$ relative to α-Fe (fig. 1) and quadrupole splitting $\overline{\Delta E_Q}$ (fig. 2) at room temperature versus boron content in amorphous iron-boron,

o sputtered on boron-nitride at RT;
● sputtered on boron-nitride at LN_2-temp.;
▽ evaporated on quartz;
△ evaporated on aluminium;
▫ data of Chien et al.[5], sputtered;
* implanted[2] Fe into cryst. B;
\+ crystalline compounds;
▱ melt-quenched ribbon.

$C_s(x)$ is the contact surface concentration of A-atoms around Fe-atoms defined by:

$$C_s(x) = \frac{(1-x)\,V_A^{2/3}}{xV_{Fe}^{2/3} + (1-x)\,V_A^{2/3}} . \tag{2}$$

Here V is the atomic volume per mole. $\delta(IS)_{max}$ is the isomer shift (relative to α-Fe) in a dilute unstrained system in which each Fe atom is surrounded by A atoms only. It is represented as:

$$\delta(IS)_{max} = P'(\phi_A^* - \phi_{Fe}^*) + Q'(n_{WS}^A - n_{WS}^{Fe})/n_{WS}^{Fe} . \tag{3}$$

The first term in eq. (3) reflects the interatomic charge transfer between atomic cells of atom A and the Fe-atoms, thereby changing the s-electron density at the Fe nucleus. A linear relationship between the change of the number of electrons (s and d together) per iron atom and the increase in the s-electron density at the Fe-nucleus is assumed. This term is determined by the difference in electronegativity or chemical potential between the cells. Instead of taking the chemical potential the macroscopic workfunction ϕ^* is used[9]. The second term of eq. (3) takes into account the intra-atomic charge redistribution on alloying, when there is a difference in electron density n_{WS} of the dissimilar atomic cells (WS is the Wigner-Seitz cell). This electron-density mismatch at the cell boundaries is removed by means of s → d electron transition. Since s-electrons reside more at the outside regions of the atomic cells than d-electrons, conversion of s-type electrons into d-type electrons results in a decrease of n_{WS}. P' and Q' are of opposite sign and within a given class of materials (Fe-base alloys) they can be regarded as constants.

For strained systems an additional term is necessary to take into account the change in isomer shift when the volumes of the iron cells change in a matrix of A atoms of different size. This volume mismatch contribution can be derived from elastic continuum considerations[7,8,10]:

$$IS_{vol} = \frac{0.615\ K_A}{0.615\ K_A + K_{Fe}} \frac{V_A - V_{Fe}}{V_{Fe}} \frac{\partial\ IS}{\partial \ln V} . \tag{4}$$

K is the bulk modulus[11].

Values of ϕ^*, n_{WS}, V and K for iron and boron are given in Table I[6,11].

TABLE I

	ϕ^*(V)	n_{WS}	V_m(cm^3)	K(10^{11} N/m^2)
Fe	4.93	5.55	7.1	1.683
B	4.75	3.72	4.7	1.78

3.3. Analysis of $\overline{IS}$ and $\overline{\Delta E_Q}$ of amorphous iron-boron.

The isomer shift $\overline{IS}$ as a function of boron surface concentration C_s is given in figure 3.

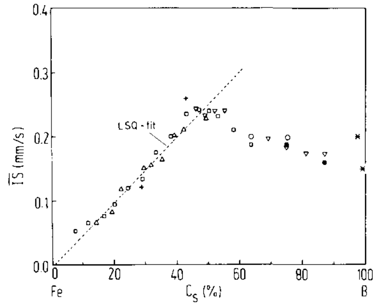

FIGURE 3
Mean isomer shift $\overline{IS}$ at room temperature (relative to α-Fe) as a function of surface concentration of boron atoms C_s in amorphous iron-boron. For legend see fig. 1 and 2.

A least squares fit to a straight line on the iron-rich side and extrapolation to $C_s = 1$ gives $\delta(IS)^{exp}_{max} = 0.50$ mm/sec.

From the Miedema-Van der Woude model without volume correction term we find (with P' = 0.66, Q' = -1.50 as determined from a fit of $\delta(IS)_{max}$ of ^{57}Fe diluted in several crystalline transition metal hosts, analogous to reference 8, 13 and 14) $\delta(IS)^{calc}_{max} = 0.38$ mm/sec. The volume mismatch contribution calculated from eq. (4) with $\frac{\partial IS}{\partial \ln V} = 1.33$ mm/sec[12] is $\delta(IS)^{calc}_{vol} = -0.18$ mm/sec. With volume mismatch term we then find for strained systems $\delta(IS)^{calc}_{max,strained} = (0.38 - 0.18)$ mm/sec = 0.20 mm/sec.

With the Miedema-Van der Woude model in mind we draw the following conclusions from figure 3:

- on the iron-rich side the amorphous Fe_xB_{1-x}-alloys are dense strainfree packed;
- for $x \lesssim 50$ a/o the volume mismatch correction term is necessary, indicating that the iron atoms occupy strained positions in the heap of boron atoms;
- implanted iron into boron also has a strained structure.

It can also be seen from figure 3 that our data of the isomer shift are in good agreement with Chien's data[5] for sputtered samples; at $x \lesssim 50$ a/o small deviations occur. This could be caused by uncertainties in the compositions of the sputtered samples. Also the substrate temperature of the sputtered samples seems to influence the value of $\overline{IS}$. As noted before, the composition of the evaporated samples is better controlled.

The contributions to the electric field gradient (which is proportional to the quadrupole splitting ΔE_Q) at the ^{57}Fe nuclei can be divided in an interatomic and intra-atomic contribution. But since the intra-atomic redistribution is usually assumed to reflect the nearest neighbour charge asymmetry, the interatomic contribution is considered as an amplification term so that only the neighbour contribution has to be calculated for the relative shape of the $\overline{\Delta E_Q}$ vs. composition dependence. The electric field gradient has been calculated[15] assuming point charges in computer simulations of quasi crystalline packings and dense random packings of hard spheres (DRPHS). We find that not only in the case of DRPHS models, as suggested by Czjek et al.[16], but also in that of quasi crystalline models the probability for $\Delta E_Q = 0$ and the asymmetry parameter $\eta = 0$ is very small. Furthermore we compute that the shape of the $\overline{\Delta E_Q}$ vs. composition is convex, in disagreement with the experiments. With the isomer shifts in mind this suggests the following conclusion from figure 2: in the iron-rich region $\overline{\Delta E_Q}$ follows the "ideal" slightly convex curve. The significant increase at the boron-rich side probably indicates that the Fe atoms are squeezed into more asymmetric atomic surroundings.

3.5. Concluding remarks

It must be noted that in Miedema's model for the description of the heat of formation of Fe with s,p-elements an additional term was necessary associated with the hybridization of the Fe 3d band with the s,p-bands of the nonmagnetic component (the so-called R-term[6,7]). It is not clear what the effect of hybridization of the iron 3d band is on the isomer shift. In cases analyzed until now the Miedema-Van der Woude model can describe the general features (e.g. the sign and trend) of the isomer shift versus composition in the amorphous iron-boron system satisfactory, although uncertainties about possible ordering effects (chemical short range order) which affect the surface concentrations still remain. To remove these uncertainties and prove the validity of the Miedema-Van der Woude model a similar examination of other amorphous systems combined with diffraction experiments, such as (energy-dispersive) X-ray diffraction, neutron diffraction and EXAFS is necessary. Photo-electron spectroscopy combined with band structure calculation could be very useful in checking the validity of the Miedema-terms.

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