

## Brief Reports

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### Packing and chemical effects in amorphous Fe-Zr and Fe-B alloys

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Mössbauer  $^{57}\text{Fe}$  isomer-shift data in amorphous  $\text{Fe}_x\text{Zr}_{1-x}$  alloys show that the atoms constitute a strain-free packing over the whole measured composition range from  $x=0.1$  to  $0.9$ . The interatomic charge transfer dominates the intra-atomic charge transfer. The charge transfer and the change in atomic radii as a function of the concentration have been calculated. In the  $\text{Fe}_x\text{B}_{1-x}$  system the structure is somewhat expanded at the iron-rich side, whereas at the boron-rich side the iron atoms are squeezed into the boron framework.

The determination of the structure of amorphous materials with diffraction techniques encounters a fundamental problem. Diffraction provides a representation in reciprocal space in which the structure of amorphous materials cannot be given. The measured interference function can be transformed into a radial distribution function, but this is only a one-dimensional representation of a three-dimensional structure.<sup>1,2</sup> For a further unraveling of the structure one has to switch to modeling with restrictions concerning packing and chemical effects.<sup>3-5</sup>

In this article we introduce a completely different approach whereby the packing and chemical effects can be studied directly. Our experimental information is obtained from isomer shift data of Mössbauer spectra. With a model recently presented<sup>6,7</sup> by Miedema and Van der Woude the various contributions related to packing and chemical bonding can be separated. In this way complementary information about the structure of amorphous models can be obtained independent of an *a priori* structural model.

The isomer shift (IS) of Mössbauer spectra is directly related to the *s*-electron density of the Mössbauer nucleus,  $^{57}\text{Fe}$  in our case, and indirectly, through shielding, to the *d*-electron density. Changes in the electronic structure upon alloying may give rise to various effects on the isomer shift, even of a compensating nature. In the above-mentioned theory for the isomer shift in alloys, only parameters derived from bulk properties of the composing elements are used. In this theory an alloying process is described with two chemical and one physical contribution to the isomer shift. The chemical contributions are (a) an

interatomic electron transfer to the more electronegative constituent proportional to  $\Delta\phi^*$ , the difference between the work functions of the two constituents, and (b) an intra-atomic *s* → *d* transfer determined by  $\Delta n_{\text{WS}}$ , the difference in the electron densities of the neighboring dissimilar Wigner-Seitz cells. The physical contribution is a volume adjustment if the atomic volumes of the partners differ. The change in the volume can be calculated with use of the elastic continuum theory of Eshelby.<sup>8,9</sup> Ingalls<sup>10</sup> also used a volume term in his analysis of the isomer shift of dilute iron alloys  $\text{FeX}$ , but did not take into account the volume relaxation of the matrix, so that this volume effect was overestimated with a factor of 2. In our IS analysis we use the same bulk parameters  $\phi^*$  and  $n_{\text{WS}}$  as a Miedema's theory for the heat of formation of binary alloys.<sup>11</sup> The need for the volume contribution is nicely illustrated in a comparison of IS of dilute and ordered gold alloys.<sup>7</sup> In dilute disordered alloys a volume readjustment between the guest and the neighboring host atoms takes place, while in ordered alloys the atoms fit strain-free into the lattice. Here we emphasize the volume contribution, because this happens to give novel information about the packing of amorphous alloys.

The Mössbauer measurements are done on  $^{57}\text{Fe}$  nuclei in amorphous  $\text{Fe}_x\text{Zr}_{1-x}$  and  $\text{Fe}_x\text{B}_{1-x}$  alloys with  $x$  between 0.1 and 0.9. The alloys are prepared in various ways: by liquid quenching around the eutectic composition  $x \approx 0.8$  for the Fe-B system and around  $x \approx 0.9$  and  $x \approx 0.25$  for the Fe-Zr system, and by sputtering or coevaporating over the whole composition range between  $x \approx 0.1$  and  $x \approx 0.90$ . The

results discussed in this paper are obtained from conversion-electron Mössbauer spectroscopy and from transmission Mössbauer spectroscopy at room temperature. Alloys of the same composition but prepared with different techniques gave very similar spectra, so that no distinction will be made. The results of the measurements are shown in Fig. 1.

For the IS analysis we can combine the two chemical contributions and write for the isomer shift of an  $^{57}\text{Fe}$  nucleus completely surrounded by atoms  $A$

$$\Delta_{\text{IS}}^{\text{max}} = P'(\phi_{\text{Fe}}^* - \phi_A^*) + Q'(n_{\text{WS}}^{\text{Fe}} - n_{\text{WS}}^A), \quad (1)$$

and the concentration dependence

$$\Delta_{\text{IS}}(x_s) = (1 - x_s)\Delta_{\text{IS}}^{\text{max}} + \Delta, \quad (2)$$

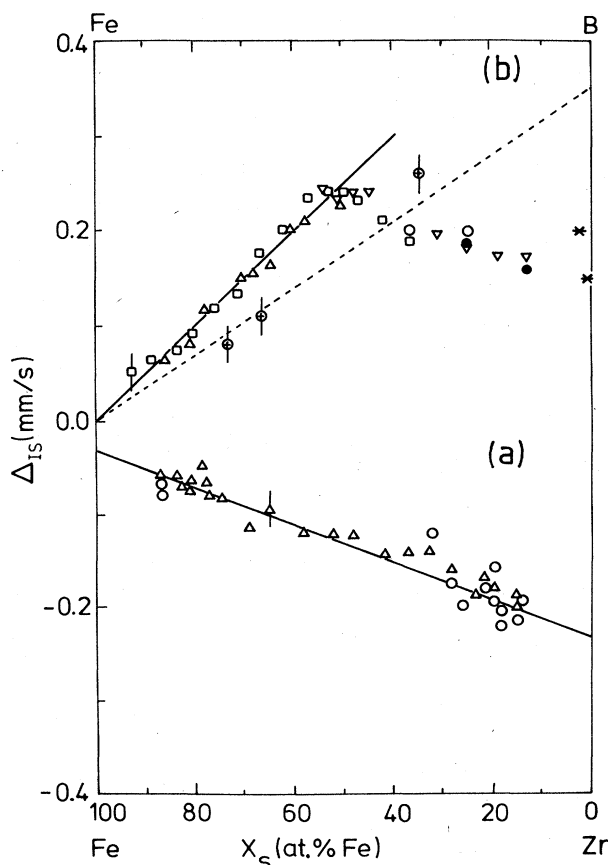


FIG. 1. Isomer shift vs surface concentration of (a) amorphous  $\text{Fe}_x\text{Zr}_{1-x}$  alloys prepared by liquid quenching (O) and coevaporation on an Al substrate ( $\Delta$ ), and (b) amorphous  $\text{Fe}_x\text{B}_{1-x}$  alloys prepared by sputtering at room temperature and liquid-nitrogen temperature (O,  $\bullet$ , respectively), and by coevaporating on a quartz and Al substrate ( $\nabla$ ,  $\Delta$ , respectively), sputtered data of Chien and Unruh, Ref. 12 ( $\square$ ) and implanted data of Sawicka and Sawicki, Ref. 13 ( $*$ ) are included also. Data of crystalline  $\text{Fe}_3\text{B}$ ,  $\text{Fe}_2\text{B}$ , and  $\text{FeB}$ , obtained from the literature (see Ref. 14) are included for comparison ( $\oplus$ ), where  $x_s$  is calculated by use of Miedema's empirical expression for intermetallic compounds, Ref. 15. The solid lines are fitted to the data; the dotted line has been calculated with use of the Miedema parameters.

TABLE I. Parameters for the calculation of the isomer shift. One density unit (d.u.) corresponds with approximately  $4.7 \times 10^{22}$  e/cm $^3$ .

	$\phi^*$ (V)	$n_{\text{WS}}$ (d.u.)	$B$ ( $10^{11}$ N/m $^2$ )	$V_m$ (cm $^3$ )
Fe	4.93	5.55	1.683	7.1
Zr	3.40	2.69	0.833	14.0
B	4.75	3.72	1.78	4.7

where the surface concentration  $x_s$  is given by

$$x_s = \frac{xV_{\text{Fe}}^{2/3}}{(1-x)V_A^{2/3} + xV_{\text{Fe}}^{2/3}} \quad (2a)$$

$x$  is the iron concentration in atom percent;  $V_A$  and  $V_{\text{Fe}}$  are the molar volumes of the  $A$  and Fe atoms, respectively.  $P'$  and  $Q'$  are constants obtained from data fitting.  $\phi^*$  is the work function and  $n_{\text{WS}}$  is the electron density in the Wigner-Seitz cell and has been calculated from  $n_{\text{WS}} = (B/V_m)^{1/2}$ , where  $B$  is the bulk modulus and  $V_m$  the molar volume.

The volume term is, again for the case of one Fe atom surrounded by  $A$  atoms, given by

$$\Delta_{\text{IS}}^{\text{vol}} = \frac{0.615B_A}{0.615B_A + B_{\text{Fe}}} (V_A - V_{\text{Fe}}) \frac{\partial \Delta_{\text{IS}}}{\partial V} \quad (3)$$

$B_{\text{Fe}}$  and  $B_A$  are bulk moduli of iron and the element  $A$ , respectively.  $\partial \Delta_{\text{IS}} / \partial V = 0.19$  mm/s cm $^3$  is obtained from the pressure dependence of the isomer shift in  $\alpha$  iron. $^{10}$  With the parameters given in Table I, this volume contribution can be calculated and the result is +0.25 mm/s for FeZr and -0.18 mm/s for FeB.

We obtained the parameters  $P' = -0.66(7)$  and  $q' = 0.26(3)$  by fitting a large number of iron alloys; these values are in reasonable agreement with those obtained by Van der Kraan and Buschow in amorphous alloys. $^{16}$  Now all the contributions to the isomer shift can be calculated and compared with the experimental results. The results of these calculations are given in Table II.

The meaning of the data shown in Table II can be discussed by considering the concentration dependence of the isomer shift as plotted in Fig. 1. For FeZr the line drawn in Fig. 1(a) is a fit to the experimental data with use of (2), which gives the maximum experimental isomer shift  $\Delta_{\text{IS}}^{\text{expt}} = -0.23$  mm/s. This experimental value is very close to the sum of the calculated chemical contributions  $\Delta_{\text{IS}}^{\text{max}} = -0.27$  mm/s. From this close agreement we conclude that in amorphous Fe-Zr alloys the volume contribution is not present. Or, in other words, the iron atoms in amorphous Fe-Zr alloys form a strain-free packing over the whole measured concentration range [Fig. 2(a)]. This is in contrast to the isomer shift in crystalline FeZr where the

TABLE II. Calculated isomer shift contributions in mm/s.

	$\Delta_{\text{IS}}(\phi^*)$	$\Delta_{\text{IS}}(n_{\text{WS}})$	$\Delta_{\text{IS}}^{\text{max}}$	$\Delta_{\text{IS}}^{\text{expt}}$	$\Delta_{\text{IS}}^{\text{vol}}$	$\Delta_{\text{IS}}^{\text{c}}$
Fe-Zr	-1.01	+0.74	-0.27	-0.23	0.25	+0.035
Fe-B	-0.12	+0.47	+0.35	+0.50	-0.18	+0.20

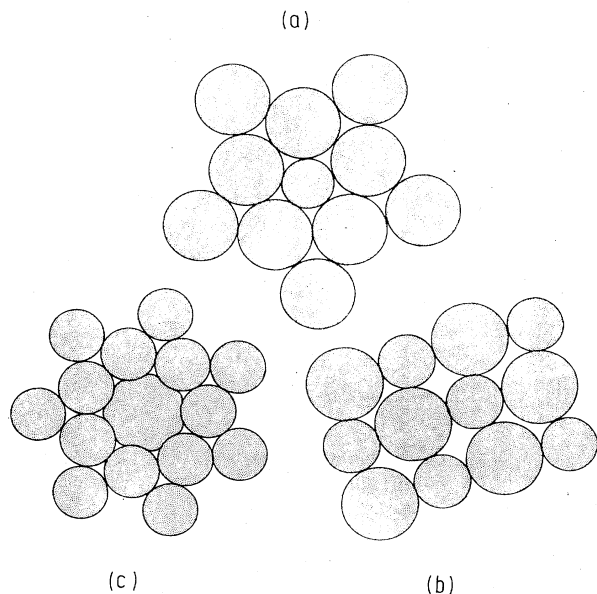


FIG. 2. Schematic two-dimensional presentations of the various packings (a) strain-free packing of Fe atoms (small circles) and Zr atoms (large circles), (b) open packing of iron atoms through covalent bonding by the smaller B atoms, and (c) iron atoms squeezed in the packing of smaller B atoms.

measured value  $\Delta_{IS}^x = 0.035$  mm/s can only be explained by adding the large volume term to  $\Delta_{IS}^{max}$ . As can be seen in Table II the two chemical contributions  $\Delta_{IS}(\phi^*)$  and  $\Delta_{IS}(n_{WS})$  are large, but the electron transfer  $Zr \rightarrow Fe$  dominates and determines the negative sign of the isomer shift.

The charge transfers and the atomic radii as a function of the concentration have been calculated with (1) and (2) and the results are shown in Table III. The partial molar volumes of the constituents have been corrected for the charge transfer by use of the model of Miedema and Niessen.<sup>17</sup> In order to calculate the atomic radii from the molar volumes we used a value for the packing fraction of 0.65. This value is in agreement with computer simulations of densely packed systems.<sup>18</sup>

We see that the charge on the Fe atom increases with decreasing Fe concentration and that the radius increases. Similar conclusions have been drawn from x-ray work on amorphous Zr-Cu and Nb-Ni alloys by Chen and Waseda.<sup>19</sup>

The results also support the conclusion from x-ray anomalous scattering measurements by Waseda and Chen<sup>20</sup> that the Zr-Zr and Zr-Fe distances are shorter than expected from Goldschmidt radii as a result of charge transfer from the Zr *d* shells.

For comparison we also show the IS data of the Fe-B system<sup>21</sup> in Fig. 1(b). These results are in agreement with the data published by Chien and Unruh.<sup>12</sup> In amorphous Fe-B alloys the intra-atomic contribution associated with the  $\Delta n_{WS}$  is most dominant and determines also the positive sign (see Table II). The electron transfer  $B \rightarrow Fe$  in Fe-B is small, so that charging effects and consequently changes in atomic radii as a function of concentration like in Fe-Zr (see Table III) are not expected in the Fe-B system. The maximum at  $x_s \approx 0.5$  in the  $\bar{\Delta}_{IS}$  vs  $x_s$  curve cannot be explained by the two chemical contributions unless we assume con-

TABLE III. Charge transfer, partial molar volumes, and atomic radii in amorphous  $Fe_xZr_{1-x}$  alloys.

$x$	$x_s$	$\Delta Z_{Fe}$ (electron charge)	$\Delta Z_{Zr}$ (electron charge)	$V_{Fe}^{cor}$ (cm <sup>3</sup> /mol)	$V_{Zr}^{cor}$ (cm <sup>3</sup> /mol)	$R_{Fe}$ (Å)	$R_{Zr}$ (Å)
0.90	0.871	0.07	-0.60	7.25	11.09	1.23	1.42
0.80	0.749	0.13	-0.53	7.40	11.44	1.24	1.43
0.60	0.525	0.26	-0.39	7.69	12.13	1.26	1.46
0.40	0.327	0.37	-0.25	7.95	12.78	1.27	1.49
0.20	0.153	0.48	-0.12	8.20	13.40	1.28	1.51
0.0	0.0	0.58	0.00	8.42	13.97	1.29	1.53

centration dependence of  $P'$  and  $Q'$ , which is not acceptable from the chemical point of view. The two chemical contributions as expressed in formulas (1), (2), and (2a) give always a straight line with a slope determined by  $P'$  and  $Q'$ . Since we have no experimental evidence to do otherwise we take the same values for  $P'$  and  $Q'$  as in a large number of iron alloys including the Fe-Zr system. This procedure results in the dotted line of Fig. 1(b) representing the theoretical contributions of the intra- and interatomic electron transfers. The possibility of attributing deviations from the straight line to a concentration dependence of the chemical interactions is not considered further, because the isomer shift in intermetallic Fe-B compounds follows the straight line rather closely [see Fig. 1(b)]. Thus the volume contribution can easily be found by taking the difference between the measured curve and the theoretical dotted line [see Fig. 1(b)]. This term, given by formula (3), expresses the effect of packing in the various concentration ranges. For example, the data points in the range of 100–50 at. % Fe lie all above this curve. This indicates a volume contribution lowering the *s*-electron density by an overall expansion of the structure. By use of  $\partial \Delta_{IS} / \partial V = 0.19$  mm/s cm<sup>3</sup>, we estimate a volume expansion of roughly 5% in the  $Fe_{0.5}B_{0.5}$  alloy [Fig. 2(b)]. In the B-rich range the isomer shift decreases with decreasing Fe content and falls clearly below the "ideal" strain-free curve, again caused by the volume contribution. From the difference of  $\Delta_{IS}^{max}$  and the value  $\Delta_{IS} = 0.18$  mm/s measured in the B-rich samples we get  $\Delta_{IS}^B \approx -0.17$  mm/s; this inserted in formula (3) gives a reduction of the atomic volume of 12% in the B-rich region [Fig. 2(a)]. So in the Fe-rich region the iron atoms are somewhat loosely packed, but with increasing B content the Fe atoms have to fit in the smaller holes of the framework of B atoms. Unfortunately, right now there are no diffraction data available, so that our conclusion cannot be checked independently like that of the Fe-Zr system.

In summary we conclude from IS versus concentration data that amorphous Fe-Zr alloys can be considered as a strain-free packing and that the isomer shift is only due to intra- and interatomic electron transfer with considerable charging effects. Since the isomer shift is sensitive to the number of neighbors only, and not to the configuration, it is not possible to do more specific statements concerning the chemical short-range order. In Fe-B alloys the IS versus concentration is more complicated, which can be attributed to various aspects of atomic volume misfit. In the Fe-rich region the Fe radius is about 2% larger than in the pure metal, while in the B-rich region the iron radius is about 4% smaller. Interatomic charge transfer is negligible in Fe-B.

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