FORMATION, THERMAL STABILITY AND PHYSICAL PROPERTIES OF AMORPHOUS 3d-BASED ALLOYS

by K. H. J. BUSCHÖW

Philips Research Laboratories, 5600 JA Eindhoven, The Netherlands

Abstract

A few technological applications of amorphous alloys are briefly discussed, stressing some unique properties of amorphous alloys. A comparative study is made of the glass forming tendency and the thermal stability in several Ni–base amorphous alloys. New experimental data for crystallization temperatures are given for amorphous alloys in which Ni is combined with Nb, Gd and Th. The occurrence of compositional short range ordering and its effect on the crystallization temperature, activation energy for crystallization, heat of formation and magnetic properties is discussed. New experimental data of the magnetic properties of amorphous Zr₁₋ₓFeₓ, La₁₋ₓNiₓ and W₁₋ₓCoₓ alloys are given. The interpretation of the magnetic properties of these alloys and of alloys reported in the literature, is made in the light of experimental results obtained by means of various techniques used to study the electronic properties of amorphous alloys.

PACS numbers: 81.50-e, 75.50kj, 71.20.+c.

1. Introduction

Many amorphous alloys have superior properties compared to their crystalline counterparts which make them suitable for various technological applications. These comprise applications as superconducting materials, starting materials for permanent magnets, materials for high frequency transformer cores or recording heads. Thin films of amorphous alloys are applied in various types of high density recording but also in corrosion resistant coatings. By way of introduction a few examples of such applications will be briefly discussed.

The application of amorphous alloys in high frequency devices and transformer cores requires low hysteresis losses. Here one may benefit from the absence of grain boundaries in amorphous alloys which usually can act as pinning centres for Bloch walls. The metastable nature of amorphous alloys offers a further advantage that can be used to improve their performance. It is well known by now that subtle atomic rearrangements can take place in amorphous alloys. These so-called structural relaxations lead to slightly enhanced stabilities and the associated activation energies are low compared to the corresponding activation energies for the amorphous to crystalline transform-
Structural rearrangements can be initiated by annealing below the crystallization temperature $T_c$. The distribution of directions associated with the atomic rearrangements is isotropic in character. But the presence of domain walls and a preferred magnetization direction within the domains induces an anisotropy in the atomic rearrangements which leads to domain wall fixing. Much improved results can be obtained by annealing in a magnetic field which reduces the hysteresis energy losses. Oblique field annealing can be shown to be useful, in particular, since it increases the number of $180^\circ$ domain walls and hence reduces the losses due to eddy currents.

Thin amorphous films based on rare earths ($R$) and either Co or Fe ($T$) are applied in high density magneto-optical recording. The suitability of these materials stems from a high positive uniaxial anisotropy which fixes the magnetization in a direction perpendicular to the film plane. This anisotropy, in combination with the strong ferromagnetic coupling between the $T$ moments and the weaker antiferromagnetic coupling between the $R$ and $T$ moments, is the reason that alloys of an appropriate $R/3d$ ratio exhibit the favourable feature of being magnetically hard at room temperature but magnetically soft at slightly higher temperatures. This feature is used for thermomagnetic writing by means of a laser beam which locally reverses the magnetization direction (see fig. 1). The presence of the positive uniaxial anisotropy is known to depend on the preparatory conditions. In Fe–based materials prepared by co-evaporation of the constituent metals it originates from column shaped

Fig. 1. Schematic representation of different types of high density recording devices based on amorphous alloys ($\varphi_k$ stands for Kerr effect read-out, $R$ for reflectance difference read-out).
Formation, thermal stability and physical properties of amorphous 3d-based alloys

microstructure. In Co-based materials made by carefully controlled sputtering it is thought to arise from a directional anisotropy in the arrangement of pairs of Co atoms. A more detailed discussion of the origin of the uniaxial anisotropy in rare earth 3d-transition metal films is given in ref. 4. High density recording can be achieved also with other types of amorphous alloys where one uses the difference in optical reflectance or transmittance between the amorphous and crystalline state (see fig. 1).

It will be clear that in order to provide a broad experimental basis for these applications and in order to have a good understanding of the physical processes involved, some fundamental research regarding the stability of amorphous alloys and their electronic and magnetic properties is desirable. In the first place one has to keep in mind that the metastable character of amorphous alloys, apart from the advantages mentioned above, has also a great disadvantage since it makes amorphous alloys go over to the stable crystalline state as a function of temperature and time. A large part of this report will therefore be devoted to thermal stability. A simple model described earlier will be discussed and applied to the many experimental data now available for Ni alloys. This will be followed by a discussion of the occurrence of Compositional Short Range Order (CSRO). Although the occurrence of CSRO strongly affects the stability of the amorphous alloy (making it less metastable) its influence on the thermal stability is only of moderate importance. Finally, it will be shown that the occurrence of CSRO is also of influence when dealing with magnetic properties.

2. Model description

In several previous publications 4,5) a simple model has been developed in which the crystallization temperature $T_x$ was described in terms of a semi-empirical relationship of the form

$$T_x = 7.5 \Delta H_h,$$  

where $T_x$ is given in K and $\Delta H_h$ in kJ per mol of the amorphous alloy $A_{1-x}B_x$. The quantity $\Delta H_h$ is the hole formation enthalpy and pertains to a hole of the same size as the smaller type of atom in the amorphous alloy $A_{1-x}B_x$. For a given alloy the hole enthalpy can easily be derived by means of the expression

$$\Delta H_h = \bar{x} \Delta H_{1v}^B (1 - \bar{x}) \left( \frac{V_B}{V_A} \right)^{\frac{5}{6}} \Delta H_{1v}^A \tag{2}$$

using the values of the monovacancy energies ($\Delta H_{1v}^A, \Delta H_{1v}^B$) and the values of the molar volumes ($V_A, V_B$) listed for almost all metals by Miedema 6). The
effective concentrations $\bar{x}_A$ and $\bar{x}_B$ are obtained from the actual concentrations by weighing these latter with the corresponding cross-sectional areas of the $A$ and $B$ atoms. Using the fact that the cross-sectional areas are proportional to $V^\frac{1}{3}$ ($V$ is the atomic volume) one has

$$\bar{x}_B = \bar{x} = x V_B^\frac{1}{3} \left[ (1 - x) V_A^\frac{1}{3} + x V_B^\frac{1}{3} \right]^{-1}; \quad \bar{x}_A = 1 - \bar{x}. \quad (3)$$

Examples in which the experimental $T_x$ values are compared with model calculations are given in the bottom part of fig. 2. The results shown in the top part of the figure stress the fact that the thermal stability of amorphous alloys is not correlated with the heat of compound formation in the corresponding binary system. Experimental results obtained for a relatively large number of different binary Ni–based systems are compared with model calculations in fig. 3.

Fig. 2. Bottom part: Comparison of the concentration dependence of the crystallization temperatures ($T_x$) in various amorphous $A_{1-x}$Ni$_x$ alloys. The data for $A = \text{Ti}$ and Nb were obtained with a heating rate $s = 50 \text{ K/min}$ on melt spun ribbons. The data for $A = \text{Sn}$ were obtained on vapour-deposited alloys with a heating rate $s = 2 \text{ K/min}$, kindly provided by Chr. Janot. The full curves represent model calculations made on the basis of eqs (1–3) given in the main text. The scales on the left and right vertical axes correspond to the relation $T_x = 7.5 \Delta H_a$, where $T_x$ is given in K and $\Delta H_a$ is given in kJ per mol alloy $A_{1-x}$Ni$_x$. Top part: Concentration dependence of the heat of formation in various $A_{1-x}$Ni$_x$ alloys $A = \text{Sn}$, Nb and Ti derived from the data published by Niessen et al. 12).
Fig. 3. Comparison of experimental $T_x$ values with calculated hole enthalpies $\Delta H_h$ in various $A_{1-x}Ni_x$ alloys. The data were taken from the following sources: $A = Nb$ (this investigation, see table I), $A = Ti$ (ref. 13), $A = Zr$ (ref. 14), $A = Hf$ (ref. 15), $A = Th,Gd$ (present investigation, see table I), $A = La, Pr$ (ref. 5). The data for $A = Sn$ were kindly provided by Chr. Janot.

**TABLE I**

Crystallization temperatures, determined at a heating rate of 50 K/min, for several Ni-based amorphous alloys considered in fig. 3.

<table>
<thead>
<tr>
<th>composition</th>
<th>$T_x$ (K)</th>
<th>composition</th>
<th>$T_x$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Gd_{1-x}Ni_x$</td>
<td></td>
<td>$Th_{1-x}Ni_x$</td>
<td></td>
</tr>
<tr>
<td>$x = 0.28$</td>
<td>547</td>
<td>$x = 0.25$</td>
<td>645</td>
</tr>
<tr>
<td>0.29</td>
<td>545</td>
<td>0.30</td>
<td>662</td>
</tr>
<tr>
<td>0.30</td>
<td>549</td>
<td>0.40</td>
<td>653</td>
</tr>
<tr>
<td>0.32</td>
<td>559</td>
<td>0.55</td>
<td>607</td>
</tr>
<tr>
<td>0.34</td>
<td>572</td>
<td>0.70</td>
<td>642</td>
</tr>
<tr>
<td>0.36</td>
<td>585</td>
<td>$Nb_{1-x}Ni_x$</td>
<td></td>
</tr>
<tr>
<td>0.40</td>
<td>551</td>
<td>$x = 0.42$</td>
<td>943</td>
</tr>
<tr>
<td>0.52</td>
<td>565</td>
<td>0.52</td>
<td>933</td>
</tr>
<tr>
<td>0.56</td>
<td>568</td>
<td>0.60</td>
<td>925</td>
</tr>
<tr>
<td>0.58</td>
<td>557</td>
<td>0.61</td>
<td>943</td>
</tr>
</tbody>
</table>
In general, the agreement between model predictions and experiment is quite satisfactory. Yet there are two unsatisfactory aspects associated with the model description.

(i) The above description of the thermal stability of amorphous alloys is based on a kinetic approach which assumes proportionality between the temperature of incipient crystallization ($T_x$) and the activation energy $\Delta E$ for viscous flow. The latter activation energy was taken to be proportional to the hole formation enthalpy ($\Delta E \propto \Delta H_h$). Calorimetric measurements make it possible to obtain experimental values for $\Delta E$ so that one can compare the experimental $T_x$ values directly with the corresponding experimental activation energies. When this is done one is faced with the rather peculiar situation that the experimental $T_x$ values are not proportional to the experimental activation energies $\Delta E$. Remarkably enough, they are proportional to the calculated values $\Delta H_h$.

(ii) One might ask the question why the predictions of the model are not affected by the occurrence of CSRO. When the heat of alloying ($\Delta H_m$) or heat of compounding ($\Delta H_c$) is strongly negative one expects the occurrence of CSRO. In such cases the average number of dissimilar neighbours is larger than that expected on the basis of a random distribution of atoms. Moreover, the degree to which CSRO occurs will be the larger, the more negative the corresponding value of $\Delta H_c$. For instance, one expects CSRO in $\text{Ti}_{1-x}\text{Ni}_x$ to be substantially higher than in $\text{Sn}_{1-x}\text{Ni}_x$ (see top part of fig. 3), although the $T_x$ values in both systems behave in satisfactory agreement with the predictions of the model.

3. Heat of formation and CSRO

Experimental evidence for the presence of compositional short range ordering in different types of amorphous alloys was obtained on several occasions. In this report we will discuss some results of calorimetric measurements. The evidence for CSRO is an indirect one but the discussion of the calorimetric results offers the advantage that a connection can be made with the relative stability of crystalline and amorphous alloys.

The values of the formation enthalpy $\Delta H_f$ for a number of Zr–Ni compounds have been plotted as a function of composition (filled circles) in fig. 4. These values were obtained by Henaff et al. by means of solution calorimetry. The open squares in fig. 4 represent the formation enthalpies of amorphous $\text{Zr}_{1-x}\text{Ni}_x$ alloys of various concentrations. These values were derived from the heat of crystallization $\Delta H_{cr}$ and from the heat of formation of the two-phase mixtures ($\Delta H_f$) in which the amorphous alloys had crystallized. Since in a given binary system the heat of formation in the two-phase region
Formation, thermal stability and physical properties of amorphous 3d-based alloys

Fig. 4. Heat of formation ($\Delta H_f$) of several Zr-Ni compound obtained by solution calorimetry (filled circles, ref. 11). The lines connecting the data points represent the enthalpies of the corresponding two-phase mixtures ($\Delta H_f$). The open squares and stars represent values for the heat of formation obtained for various amorphous alloys (see text).

varies linearly between the $\Delta H_f$ values of the two adjacent compounds one may obtain these $\Delta H_f$ values relatively easily by interpolation (see fig. 4). For three amorphous alloys Henaff et al. determined the $\Delta H_f$ values of the amorphous alloys also by direct calorimetric measurements. These values are presented by stars in fig. 4. There is satisfactory agreement between the two sets of $\Delta H_f$ values for the amorphous alloys.

The dependence of $\Delta H_f$ on concentration for binary alloys $A_{1-x}B_x$ can be represented by means of the expression\(^{12}\)

$$\Delta H_f = 2 F(x) [(1 - x) V_A^\alpha + x V_B^\alpha] C,$$

where $C$ is a constant for a given choice of $A$ and $B$ components. The function $F(x)$ is equal to $F_C(x) = \bar{x}_A \bar{x}_B [1 + 8(\bar{x}_A \bar{x}_B)^2]$ in the case of compound formation. For regular solid solutions and amorphous alloys it reduces to $F_A(x) = \bar{x}_A \bar{x}_B$. For the crystalline compounds, eq. (4) in combination with $F_C(x)$ gives a smooth line passing through the data points in fig. 4 (filled circles). For the sake of clarity this line was not included in the figure since it does not differ much from the lines connecting the data points. For the amorphous alloys eq. (4) in combination with $F_A(x)$ gives the broken curve in fig. 4 after this curve has been shifted in the positive direction by 5 kJ/mol. This
shift may be somewhat arbitrary. It takes account of the fact that the concentration dependence of $\Delta H_f$ for the amorphous alloys should be given with respect to amorphous Zr and Ni rather than with respect to the crystalline metals Zr and Ni. This enthalpy difference was estimated to be of the order of 5 kJ/mol\(^1\)). Inspection of the results in fig. 4 makes it clear that the enthalpy values found for the amorphous alloys tend to be close to the values expected for crystalline materials. This is the case in particular for alloys of a concentration near $x = 0.6$, where the difference from the shifted solid solution curve (broken line) is quite distinct and indicates the occurrence of appreciable short range ordering. This can also be seen by direct comparison of the experimental values of the ratios $\Delta H_f$ (cryst) $- \Delta H_f$ (amorph)/$\Delta H_f$ (cryst) = $\Delta H_{cr}/\Delta H_f$. It follows that the enthalpies of the amorphous state are about 30% lower than those of the crystalline state near $x = 0.2$. But they are only less than 10% lower near $x = 0.6$.

4. Glass forming ability, thermal stability and their relation to binary phase diagrams

Three different Ni-based binary systems are compared in fig. 5. The experimental data for the crystallization temperatures are given at the top. Experimental values of the activation energies, derived from rate-dependent measurements, are given in the middle. More details regarding these experimental data were presented elsewhere\textsuperscript{13-16}. General features of the phase diagrams (in arbitrary units) are shown at the bottom\textsuperscript{16}. Note that in order to assess possible relationships between $T_x$, $\Delta E$ and features of the phase diagram fully we have used complete scales rather than truncated scales to represent the concentration dependences of $T_x$ and $\Delta E$.

It has been generally accepted that regions of so-called easy glass formation are situated around the concentrations corresponding to deep eutectics, where the depression of the melting point from the ideal solid solutions liquidus is relatively high (see, for instance, ref. 17). The three $A_{1-x}$Ni\(_x\) systems considered in fig. 5 seem to be no exception in this respect. By contrast, the results given at the top of fig. 5 show that the crystallization temperatures ($T_x$) are rather insensitive to the details of the phase diagram. The temperatures $T_x$ generally tend to increase with Ni content, which is in accordance with the predictions of the model (broken line). In all three systems one finds no enhancement of $T_x$ in the region of the deepest eutectic temperatures. This means that one cannot speak of a correlation between the thermal stability (as measured by $T_x$) and the glass-forming ability. This result can also be expressed by saying that alloys lending themselves to easy vitrification do not have better thermal stabilities than alloys that are less prone to vitrification.
Formation, thermalstability and physical properties of amorphous 3d-based alloys

Fig. 5. Comparison of the crystallization temperature $T_x$ (top), activation energies $\Delta E$ (middle) and phase relationships (bottom) in three $A_{1-x}Ni_x$ systems. For more details see refs 13-15.
The quantities $T_x$ and $\Delta E$ both reflect the thermal stability of amorphous alloys. It is noteworthy that the trends shown by the concentration dependences of $\Delta E$ are mimicked only to a very small extent by the concentration dependences of the corresponding $T_x$ values. The latter values give rise to only moderate excursions (about 10%) from the model predictions while the activation energies sometimes vary by more than 100%. It has already been mentioned above that according to the kinetic approach $T_x$ and $\Delta E$ are proportional to each other\(^7-8\)). This is a consequence of the diffusion constant being proportional to the reciprocal of the viscosity ($\eta = \eta_0 \exp \Delta E/S_e T$). Viscous flow and subsequent crystallization become possible when a critical value ($\eta_{cr} \approx 10^{13}$ Pa) is reached, leading to the relation

$$T_x \propto \frac{\Delta E}{S_e}.$$  \hspace{1cm} (5)

In deriving this expression it is usually assumed that the configurational entropy $S_e$ is a temperature-independent constant since crystallization takes place in temperature ranges well below melting temperatures. In previous analyses\(^4-5\)) the possibility of the occurrence of compositional short-range ordering was not taken into consideration. The large negative values of the enthalpy of alloying for all three systems favours the occurrence of CSRO, and some of the experimental evidence for it has been discussed in the previous section. When CSRO does occur $S_e$ may no longer be regarded as temperature-independent. In the same manner as found in atomic order-disorder transformations in crystalline alloys, one would expect the configurational entropy to give rise to reversible temperature variations in particular in alloys with CSRO. Irreversible changes in amorphous alloys were studied by Chen\(^7\), who showed that the associated temperature variation of $S_e$ leads to apparent values of the activation energy ($\Delta E$) that are larger than the actual values ($\Delta E_a$) by a factor $[1 + (\frac{d}{d T}) (\ln S_e)] / (\frac{d}{d T})$. The same applies to reversible changes of $S_e$. This means that even in the absence of irreversible changes, an enhancement of the $\Delta E$ values may be expected in alloys with CSRO. There is ample experimental evidence for the occurrence of reversible as well as irreversible changes in a number of different amorphous alloys\(^18-19\)). It can be concluded from the results discussed above that the linear relationship between $T_x$ and the experimental values of $\Delta E$ may break down in alloy systems exhibiting CSRO.

From the concentration dependence of $\Delta E$ shown for the three systems in fig. 5 one may infer that the degree of CSRO is comparatively high in the middle concentration regions. When amorphous alloys are no longer considered as having atomic arrangements of basically random distributions, alloys
of a different degree of CSRO will also have different values for $S_e$. From eq. (5) it then follows that in the middle concentration ranges mentioned above one would expect $S_e$ to be comparatively low. As a result, the corresponding $T_x$ values would be comparatively high. The effect of a lower $S_e$ value may be counteracted, however, by a low activation energy $\Delta E_0$. Here one has to consider that CSRO leads to a larger number of dissimilar neighbour atoms than would have been present in a completely random alloy and that the motion of Ni atoms in a surrounding rich in Ti, Zr or Hf is easier than in a Ni–rich surrounding. The effect of CSRO is therefore to lower $\Delta E_0$. Owing to the mutually compensating influence of both effects one may expect that the occurrence of CSRO will not much affect the predictions of the hole model. If one disregards possible differences in the crystallization temperature associated with differences in the crystallization models of the various alloys, and ascribes the variations around the calculated concentration dependences (broken lines) exclusively to CSRO, one finds that these variations are of the order of 10% in the cases of Zr–Ni and Hf–Ni and only 5% in the case of Ti–Ni. These relatively small variations are to be compared with variations of more than 100% in the case of $\Delta E$ (see the middle parts of fig. 5). Of course, one has to keep in mind that the extreme sensitivity of $\Delta E$ towards CSRO is the result of the fact that $\Delta E$ does not probe $S_e$ itself but rather its logarithmic temperature derivative.

5. Electronic properties

Information regarding the electronic properties of amorphous alloys can be obtained by means of the same techniques currently used for crystalline materials. These techniques comprise photoemission and Mössbauer spectroscopy, NMR, ESR and measurements of the magnetic susceptibility and the low-temperature specific heat. The random nature of the atomic arrangements in amorphous alloys leads to a certain degree line of broadening which is particularly pronounced in NMR experiments and the data analysis requires special care in cases where local density of states are probed by means of Knight shift measurements. In ESR experiments on Gd-doped amorphous alloys the linewidths $(\Delta H)$ range from about 150 G in amorphous Pd$_{1-x}$Si$_x$ alloys to more than 1000 G in amorphous Zr–based alloys$^{20-21}$. However, in all these cases, experiments are sufficiently accurate to separate the residual linewidths $(\Delta H_o)$ from the Korringa rates $(d(\Delta H)/dT)$. Based on the latter data values of the density of d–band states were obtained. Results obtained for various Zr–based amorphous alloys have been listed in table II$^{20}$. There is satisfactory agreement of these data with those obtained by means of specific heat measurements made on several of similar Zr–based amorphous alloys$^{22-23}$. All these
### TABLE II

Experimental values of the Korringa rate (in GK⁻¹) in various amorphous alloys and the corresponding value of the d-electron density of states (in eV⁻¹ per atom per spin).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>d(ΔH)/dT</th>
<th>Nd(E_F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr₀.₇₂Cu₀.₂₈</td>
<td>36.2</td>
<td>0.90</td>
</tr>
<tr>
<td>Zr₀.₆₀Cu₀.₄₀</td>
<td>25.5</td>
<td>0.73</td>
</tr>
<tr>
<td>Zr₀.₄₄Cu₀.₅₆</td>
<td>27.0</td>
<td>0.76</td>
</tr>
<tr>
<td>Zr₀.₃₈Cu₀.₆₂</td>
<td>22.8</td>
<td>0.70</td>
</tr>
<tr>
<td>Zr₀.₆₇Ni₀.₃₃</td>
<td>39.1</td>
<td>0.94</td>
</tr>
<tr>
<td>Zr₀.₆₇Pd₀.₃₃</td>
<td>30.1</td>
<td>0.82</td>
</tr>
<tr>
<td>Zr₀.₇₆Pt₀.₂₂</td>
<td>37.2</td>
<td>0.92</td>
</tr>
<tr>
<td>Zr₀.₆₇Co₀.₃₃</td>
<td>30.0</td>
<td>0.82</td>
</tr>
<tr>
<td>Zr₀.₇₄Rh₀.₂₆</td>
<td>35.4</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Experimental data have in common that they show that the d-electron density of states in amorphous Zr-rich alloys is larger than in crystalline Zr metal itself. It is interesting to compare these results with bandstructure calculations and results obtained by means of photoemission spectroscopy. Upon alloying the d–bands of Zr and the late transition metal T do not coalesce into a common band. Both d–bands tend to become narrower and the repulsion between the d–bands leads to a shift to higher and lower energies for the d–states of Zr and T, respectively. Furthermore it follows from the bandstructure calculations that the partial d–density of states of Zr has a minimum slightly above E_F and increases below E_F. Owing to the d–band repulsion one would expect therefore that as a consequence of the Zr d–band shift towards higher energies the Fermi level would move into a region of a higher d–density of states. This is exactly what the data in table 2 and the specific heat data suggest, since they indicate an increase in Nd(E_F) in the amorphous alloys relative to pure Zr metal.

Useful information regarding the bonding in amorphous alloys can often be obtained from results of Mössbauer spectroscopy. The Mössbauer isomer shift is a direct measure of the electronic charge density at the nuclear site of a given Mössbauer isotope and its changes observed upon alloying can provide valuable information regarding the concomitant changes in electronic properties. A systematic analysis of the Isomer Shift (IS) was first given by Miedema and van der Woude and applied to Au–alloys and compounds. Recently their model was also applied to amorphous Fe–alloys. If δ(IS)_{max} is the IS...
Formation, thermal stability and physical properties of amorphous 3d-based alloys

(relative to α-Fe) in a dilute system where each Fe atom is surrounded by A atoms only, the formula used in the data analysis can be represented by:

$$\delta(\text{IS})_{\text{max}} = 0.75 \Delta \phi^* - 1.65 \frac{\Delta n_{\text{WS}}}{n_{\text{WS}}}.$$  \hspace{1cm} (6)

Values for the electronegativity differences $\Delta \phi^* = \phi_A^* - \phi_{\text{Fe}}^*$ and the electron density difference $\Delta n_{\text{WS}} = n_{\text{WS}}^A - n_{\text{WS}}^\text{Fe}$ can be obtained by means of the data tabulated for all metals by Niessen et al.12).

In practice the strainfree dilute limit $\delta(\text{IS})_{\text{max}}$ is reached when $x \rightarrow 0$, i.e. it can be determined by means of measurements on various metals A containing Fe impurities. In dilute crystalline alloys these Fe impurities occupy crystallographic position of the A atoms in the host lattice which entails a size mismatch. This size mismatch can introduce a considerable error in the determination of $\delta(\text{IS})_{\text{max}}$. In this respect amorphous alloys represent suitable materials since there is virtually no difference between A and Fe sites. Although amorphous alloys with very low Fe concentrations cannot be prepared, the values of $\delta(\text{IS})_{\text{max}}$ can easily be obtained via measurements on less dilute alloys by extrapolation to $x \rightarrow 0$ where $x$ is an effective concentration (see eq. (3)) which measures the fractional area of contact of Fe atoms with other Fe atom neighbours. In the extrapolations mentioned use is made of the linear dependence of the IS on the effective concentration of the A component in $A_{1-x}\text{Fe}_x$

$$\delta(\text{IS})_{\text{max}} = (1 - \bar{x}) \delta(\text{IS})_{\text{max}}.$$  \hspace{1cm} (7)

The advantages of this type of analysis can be summarized as follows:

(i) It applies to a large variety of different amorphous alloys. This is illustrated by means of fig. 6 where the experimental values26) of $\delta(\text{IS})_{\text{max}}$ and values tabulated for $\phi^*$ and $n_{\text{WS}}$ have been used to plot $\delta(\text{IS})_{\text{max}}/\Delta \phi^*$ versus $\Delta n_{\text{WS}} / [n_{\text{WS}}^A \Delta \phi^*]^{-1}$. The slope and the intercept on the vertical axis correspond to the coefficients of the two terms on the right hand side of eq. (6).

(ii) Experimental values of IS can be broken down in two contributions comprising the interatomic charge transfer term $C.T = 0.75 \Delta \phi^*$ and the intra-atomic d–s electron conversion term $E.C = 1.65 \Delta n_{\text{WS}} / n_{\text{WS}}^\text{Fe}$. Using simple scaling laws these contributions can easily be translated into electron numbers26).

As an example, let us consider the situation in amorphous Zr$_{1-x}$Fe$_x$. It can be inferred from the results shown in fig. 7 that the critical concentration for the occurrence of a moment on the Fe atoms in Zr$_{1-x}$Fe$_x$ is just below $x = 0.4$. This corresponds to $\bar{x} = 0.3$. It can be derived from eqs (6) and (7) that at this concentration the charge transfer from Zr to Fe equals 0.5 electrons, the s–d conversion being even smaller (less than 0.2 electrons per Fe atom). It follows
from these results that the reduction in Fe moment from 2.2 \( \mu_B \) in Fe metal to zero in Zr\(_{0.6}\)Fe\(_{0.4}\) is not the result of a filling up of the 3d band due to charge transfer from Zr to Fe.

Fig. 6. Analysis of the experimental values of the strain-free dilute limit of the \(^{57}\)Fe isomer shift in various amorphous alloys in terms of eq. (6) (see text). Data were taken from ref. 26.

Fig. 7. Temperature dependence of several amorphous Zr\(_{1-x}\)Fe\(_x\) alloys made by melt spinning. The measurements were made in an applied field of 240 kA/m, using an adaption of the Faraday method.
It is interesting to compare the results of the $^{57}$Fe isomer shift analysis with those obtained from photoemission experiments. This comparison can be made by means of the data listed in Table III for the compound Zr$_3$Fe. Like in amorphous alloys the fractional areas of contact of an Fe atom with Zr and Fe neighbours differ from the actual atomic fractions $x$ in Zr$_{1-x}$Fe$_x$. In inter-

### Table III

Comparison of the experimental values determined from XPS core level shifts and $^{57}$Fe Mössbauer spectroscopy for the changes of the number of s,p-electrons ($\Delta n_{sp}$) and d-electrons ($\Delta n_d$) when Fe is compounded with Zr in Zr$_3$Fe.

<table>
<thead>
<tr>
<th>Method</th>
<th>$\Delta n_{sp}$(el./Fe)</th>
<th>$\Delta n_d$(el./Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS</td>
<td>+0.4</td>
<td>+0.5</td>
</tr>
<tr>
<td>$^{57}$Fe(IS)</td>
<td>+0.4</td>
<td>+0.3</td>
</tr>
</tbody>
</table>

metals like Zr$_3$Fe, which have a strong heat of formation, there is a tendency of the Fe atoms to have exclusively Fe nearest neighbours. It can be shown that owing to this feature and owing to the relatively large size of the Zr atoms one has a situation in Zr$_3$Fe which corresponds virtually to the dilute limit ($\bar{x} = 0$). From the analysis of the Mössbauer data in terms of eqs (6) and (7) one derives an increase in s,p-electrons due to charge transfer equal to C.T = 0.7 electrons per Fe, and a decrease in s,p-electrons due to s–d conversion equal to E.C = 0.3 electrons per Fe. This means that the effective increase in s,p-electrons is equal to $\Delta n_{sp} = 0.4$ el./Fe, while $\Delta n_d \approx 0.3$. These numbers are in good agreement with those derived from an analysis of the XPS core level data. The results shown in Table III make one point quite clear. There is only a charge transfer of a few tenths of an electron from Zr to Fe even in the case of high Zr concentrations. Although the experimental results of XPS and IS pertain to Fe–based alloys, there is evidence that the situation is much the same in other alloys of 3d–metals with more electropositive metals such as the rare earths and actinides.

6. Magnetic properties

The large atomic disorder and the concomitant absence of lattice periodicity in amorphous solids cause these latter materials to have magnetic properties which are different from those found in their crystalline counterparts. Results for several amorphous La$_{1-x}$Ni$_x$ alloys are shown in fig. 8. It is seen that the transition from the paramagnetic to the ferromagnetic state is rather sluggish.
The flattening of the temperature dependence of the magnetization in random systems was discussed extensively elsewhere\(^\text{30}\).

The formation of amorphous alloys in which 3d-metals are combined with more electropositive metals leads generally to a reduction in the 3d-atom moment. Examples of experimental results shown for Ni, Co and Fe alloys are discussed in refs 4, 26 and 29–32. Whereas the Ni- and Co–based amorphous alloys have a concentration dependence of the 3d–moment that extrapolates to the moment of the pure crystalline 3d–metals (\(\bar{x} \to 1\)) one often finds a different situation in amorphous Fe–based alloys. This is also the case in amorphous Hf\(_{1-x}\)Fe\(_x\) where the extrapolation would lead to a value significantly below the value 2.2 \(\mu_B/\text{Fe}\) found in \(\alpha\)--Fe \(^\text{31}\). Most likely this result is explained in terms of a distribution of exchange interactions between the 3d–moments\(^\text{33}\). In the case of Fe–based alloys one may expect a substantial portion of negative exchange interactions to be present which causes deviations from colinear ferromagnetic ordering and entails a relatively too small net saturation magnetization when determined from bulk magnetization measurements. In comparing the moment reduction in amorphous Fe–based alloys it is therefore desirable not to rely too heavily on the results of bulk magnetic measurements but to use the results derived from \(^{57}\text{Fe}\) hyperfine field measurements instead.

Fig. 8. Temperature dependence of the magnetization (measured at \(H = 240\) kA/m) of three amorphous La\(_{1-x}\)Ni\(_x\) alloys made by co-evaporation of La and Ni.
Formation, thermal stability and physical properties of amorphous 3d-based alloys

It has already been mentioned briefly in sec. 5 that a description of the moment reduction in various amorphous 3d-based alloys is often given in terms of a charge transfer model. Upon alloying, electrons are transferred from the less electronegative $A$ component to the 3d-component where they fill up the 3d-band and thus lower the 3d-moment. It is misleading that the charge transfer model, when applied to a certain class of alloys, is able to account reasonably well for the experimental data. The model is, however, less satisfactory when applied to alloys differing widely in components and composition. One of the reasons for this is probably the presence of still another effect which overrules the effect of charge transfer on the magnetic properties, which will be discussed below. Another reason is that the amount of the charge transferred from the nonmagnetic component $A$ to the transition metal $T$ in $A_{1-x}T_x$ is actually rather small, i.e. it is of the order of a few tenths of an electron (see sec. 5). In descriptions based on charge transfer the electron numbers needed are much higher. For instance Heiman and Kazama had to assume a charge transfer equal to 2.21 electrons per Zr atom in Zr$_{1-x}$Co$_x$ in order to give an adequate description of the corresponding concentration dependence of the 3d-moment$^{34)}$. In view of the experimental evidence presented at the end of sec. 5 one may conclude therefore that charge transfer does occur to some degree but that its magnitude is too small to explain the moment reduction. For this reason we will focus our attention on another mechanism that may be employed for describing moment variations in 3d-metal systems.

Based on the ideas that the degree of atomic short range order is not the same in all amorphous alloys a model has been proposed for describing the differences in magnetic properties of various amorphous 3d-based alloys$^{26,31)}$: In order to take account of the size differences that may arise between $A$ and $T$ in $A_{1-x}T_x$, only alloys of similar effective concentration $\bar{x}$ were compared. For a fixed 3d-element these alloys are expected to have the same average $T$ moment when CSRO is absent. Depending on the nature and the degree of CSRO substantially different values for the average $T$ moment will arise. Qualitatively, the nature and the degree of CSRO was estimated by the sign and magnitude of the heat of alloying or heat of compounding ($\Delta H$)$^4)$. Negative values of $\Delta H$ in amorphous alloys $A_{1-x}T_x$ will lead to average atomic arrangements in which the number of dissimilar nearest neighbours is larger than would be the case in a statistical atomic distribution. In these cases the average $T$ moment is relatively low. The reverse arguments apply if $\Delta H$ is positive. By using the sign and magnitude of $\Delta H$ as a measure of, respectively, the nature and degree of CSRO it has been possible to analyse successfully the magnetic properties of various ferromagnetic amorphous alloys in which a
Fig. 9. a) Average effective hyperfine field $|\Delta H_{\text{eff}}|$ (full circles, left scale) and average Fe moment (full squares, right scale) in amorphous $A$–Fe alloys with effective Fe concentration $\bar{x} = 0.5$ versus heat of formation. b) Average Ni moment in various amorphous Ni alloys ($\bar{x} = 0.80$) versus heat of alloying. Data were reproduced from refs 26 and 31.
Formation, thermal stability and physical properties of amorphous 3d-based alloys

3d-metal is combined with a nonmagnetic partner element. Results for Fe and Ni alloys are shown in fig. 9, where we used the data of Niessen et al.\textsuperscript{12} for obtaining $\Delta H$. All the alloys in the same figure have the same effective concentration (i.e. the 3d-atoms would have a similar fractional area of contact with other 3d-neighbours in all these alloys if CSRO were absent). The degree of CSRO, in which the 3d-atoms are surrounded by more than an average number of $A$ neighbours, is expected to increase in going from Mg to Zr. As a consequence the average 3d-moment of the alloys decreases.

In this model the effect of CSRO on the magnetic properties is overemphasized and no account has been taken of the fact that there may be differences in the moment reducing power between the various $A$ components in alloys of the same effective concentrations $\bar{x}$. In fact, the descriptions based on CSRO and the Friedel model discussed elsewhere\textsuperscript{31} may be regarded as being supplementary to each other. The alloys with $T = Nb, V$ and Mo in fig. 9a represent examples where the moment reducing power is expected to be particularly high. This is probably the reason why they fall outside the broad band containing the other alloys.

7. Concluding remarks

In this report the effect of CSRO on various physical properties of amorphous 3d-based alloys has been discussed. Calorimetric measurements have shown that the absolute value of the formation enthalpy of amorphous alloys may be smaller than that of the crystalline state by about $30\%$ when CSRO is small or absent. In the presence of CSRO this enthalpy difference can become much smaller (less than $10\%$).

The transformation temperature of the amorphous-to-crystalline transition defining the resistance against crystallization of amorphous alloys is not much affected by CSRO. By contrast, the (apparent) activation energies for crystallization obtained from rate-dependent measurements may change appreciably when CSRO is present. It was also found that amorphous alloys of a composition corresponding to the lowest eutectic composition in a binary system, where the depression of the melting point from the ideal solution liquidus and the glass-forming ability are highest, are not necessarily characterized by a high thermal stability.

The effect of CSRO in 3d-based alloys is to change the fractional number of nearest 3d-atom neighbours. When the degree of CSRO is taken to increase with increasing heat of alloying one finds a correlation between the average 3d-moment and the correspondent heat of alloying.
REFERENCES