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Experimental Study of the Structure of Ni-Zr Metallic Glasses

Ъy

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July 1993

A Thesis submitted to the Faculty of Graduate Studies and Research in partial fulfillment of the requirements for the degree of Doctor of Philosophy

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Abstract

This thesis presents a structural study of Ni-Zr metallic glasses. It is the first time that a careful complete and systematic investigation into the structure of a glassy metallic system has been carried out. The results have improved our understanding of the structure of metallic glasses and clarified confusion in previous studies. The total structure factors of melt-spun and sputtered amorphous $Ni_{x}Zr_{1-x}$, $0.25 \le x \le 0.86$, were obtained with an accuracy of 1-4%. Accurate partial structure factors of Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} were obtained using x-ray and neutron diffraction while those of Ni_{0.33}Zr_{0.67} were also obtained independently using isomorphous substitution. The results confirmed the reliability of the isomorphous substitution method for Ni-Zr glasses. We have found a strong correlation between the local atomic structure and the electron transport properties of Ni-Zr glasses. No structural difference between melt-spun and sputtered Ni-Zr glasses was found. Our results show that the Faber-Ziman partial structure factors of Ni-Zr glasses is strongly composition dependent. The local topological order in amorphous Ni_{0.33}Zr_{0.67} is found to be quite similar to that in the BCT NiZr₂ compound whereas a discrepancy in the structure is found between amorphous Ni_{0.67}Zr_{0.33} and the FCC Ni₂Zr compound. Our results have also shown that the Ni-Zr glasses are an almost random mixture of Ni and Zr atoms and that there is no correlation between the pre-peak in the neutron structure factor and the chemical short-range order in the metallic glass.

Résumé

Cette thèse présente une étude structurale des verres métalliques de Ni-Zr. Pour la première fois, une investigation soignée, complète et systématique de la structure d'un système de verre métallique a été accomplie. Ces résultats ont amélioré notre compréhension de la structure des verres métalliques et clarifiés la confusion existant dans les études précédentes. Les facteurs de structure totaux des systèmes de Ni_x Zr_{1-x} , 0.25 $\leq x \leq$ 0.86, péparés par "melt-spinning" ou par grésillement, ont été obtenus avec une précision de 1-4%. Des facteurs de structure partiels précis du Ni_{0.33}Zr_{0.67} et du Ni_{0.67}Zr_{0.33} ont été obtenus par diffusion des rayons-x et par diffusion de neutrons alors que ceux du Ni_{0.33}Zr_{0.67} ont été aussi obtenus indépendamment par substitution isomorphe. Les résultats confirment la sûreté de la méthode de substitution isomorphe pour les verres de Ni-Zr. Nous avons trouvé une forte corrélation entre la structure atomique locale et les propriétés de transport électroniques des verres de Ni-Zr. Aucune différence structurale entre les verres préparés par "melt-spinning" et par grésillement n'a été découverte. Nos résultats montrent que le facteur de structure partiel de Faber-Ziman des verres de Ni-Zr dépend directement de la composition. L'ordre topologique local du Ni_{0.33}Zr_{0.67} amorphe est très similaire à celui que l'on trouve dans le composé tétragonal centré de NiZr₂ tandis qu'une discordance est trouvé entre le Ni_{0.67}Zr_{0.33} amorphe et le composé cubique à face centrée de Ni₂Zr. Nos résultats ont montré que les verres de Ni-Zr sont presque des mélanges aléatoires d'atomes de Ni et de Zn et qu'il n'y a aucune corrélation entre le pré-pic dans le facteur de structure obtenu par diffusion de neutrons et l'ordre chimique à courte portée dans le verre métallique.

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I dedicate this thesis to my dear husband, Liao Le Xiang.

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Chapter 1 Introduction

Metallic glasses are alloys in which the atoms show no long range order. They are also called amorphous alloys or non-crystalline alloys. The first report in which amorphous alloys were claimed to have been made was by Kramer [1,2]. These alloys were made by vapor deposition. Brenner et al. [3] later claimed to have made amorphous NiP alloys by electrodeposition. In 1960, Duwcz et al. discovered a method of preparing amorphous alloys by direct quenching from the melt [4]. The solidification occurs so rapidly that the atoms are frozen in their liquid configuration. As schematically shown in figure 1.1, in both the liquid and amorphous state, the atoms are randomly distributed in a nearly close-packed structure, and the mean free path is short and comparable to the atomic size. This means that the positional correlation of atoms is relatively strong within the near-neighbor region. Unique mechanical, corrosion, electrical and magnetic behavior results from this short-range order structure [5]. For example, the electrical resistivities of these materials are three or four times higher than those of conventional polycrystalline iron or iron-nickel alloys; the materials can be exceptionally hard and have extremely high tensile strengths; some amorphous alloys are exceptionally corrosion resistant while others behave as very soft magnetic materials. These properties individually and in combination have stimulated wide scientific and technological interest.

In physics, amorphous solids can be thought of as a new state of matter, complementary to the traditional gas, liquid, and crystalline solid states. Although interest in amorphous solids has increased considerably in recent years, due to their technological significance, the amorphous solid state is still very much less understood at a microscopic level than the crystalline solid state. The lack of periodicity and long range order in an amorphous solid means that there is no simple structural formalism which can be used in the calculation of microscopic properties. However, for a completely random system, the microstructure can be described by a one dimensional probability function, called the atomic pair distribution function,

$$g(r) = \frac{\rho(r)}{\rho_o} \tag{1.1}$$

where $\rho(r)$ is the atomic correlation function and ρ_o is the average number density. Therefore, g(r) shows the deviation from the average number density. One can not directly measure the g(r) function, but its Fourier transform, the structure factor, can be measured through x-ray, neutron, or electron diffraction experiments.

As with crystalline solids, the major structural probes for non-crystalline materials are x-ray and neutron diffraction. The detailed relation between the diffraction data and the structure of non-crystalline systems has been previously discussed in the literature [7-10]. The diffraction intensity $I(\theta)$ reveals the interference effects between the radiation scattered by different atoms in the material. By normalizing $I(\theta)$ to the intra-atomic scattering intensity, $\langle f^2 \rangle$, a dimensionless quantity S(Q)



Figure 1.1: Schematic diagram of atomic distribution, pair distribution function g(r)and structure factor S(Q) in the gas, liquid, amorphous, and crystal states (Taken from reference [6]).

is obtained ¹

$$S(Q) = \frac{I(\theta)}{\langle f^2 \rangle}$$
(1.2)

where, $Q = 4\pi \sin\theta/\lambda$, is the momentum transfer associated with the scattering angle 2 θ . S(Q) is called the "structure factor". Because the division by $\langle f^2 \rangle$, the structure factor is determined entirely by the microscopic structure, independent of the type of atoms in the material. The structure factor is related to the atomic pair distribution function g(r) through the following Fourier transform:

$$S(Q) = 1 + \rho_o \int_0^\infty [g(r) - 1] exp(-i\mathbf{Q}\mathbf{r}) d\mathbf{r}$$
(1.3)

Figure 1.1 shows schematically the structure factor S(Q) and the atomic pair distribution function g(r) for a gas, liquid, and amorphous and crystalline colids. For a multi-component system, this method of normalization results in the "total structure factor", which is the summation of the "partial structure factors", $S_{ij}(Q)$

$$S(Q) = \sum_{i,j} w_{ij} S_{ij}(Q) \tag{1.4}$$

where both i and j summations are taken over atom types, and the weighting factors can be expressed as functions of atomic concentrations, c_i and c_j , and the atomic form factors, f_i and f_j :

$$w_{ij} = w_{ij}(c_i, c_j, f_i, f_j)$$
 (1.5)

It has become recognized that one of the most important quantities characterizing a non-crystalline material are the partial structure factors. Their Fourier transforms result in the partial atomic pair distribution functions, $g_{ij}(r)$. Therefore, A accurate

¹For simplicity, the definition due to Ashcroft and Langreth [11] is used here. Throughout this work, however, two other definitions of the structure factor are used, one is due to Faber and Ziman [12], and the other due to Bhatia and Thornton [13]. For multi-component systems, these three formalisms give different sets of partial structure factors which can be mutually transformed by linear relations.

knowledge of the partial structure factors is essential for a quantitative understanding of not only the structure, but also various other properties of non-crystalline solids.

Recent advances in both diffraction theory and experimental techniques allow a complete structural determination of non-crystalline solids in terms of structure factors [14,15]. In addition to conventional x-ray and neutron diffraction, other relatively new techniques have been used, such as anomalous x-ray scattering, time-offlight (TOF) pulsed neutron scattering, neutron isotopic substitution, x-ray isomorphous substitution, and finally, extended x-ray absorption fine structure (EXAFS). Almost all amorphous materials are multi-component systems. According to equation 1.2, the structure of a binary system is characterized by three partial structure factors: two like atom pairs, $S_{ii}(Q)$ and $S_{jj}(Q)$; and one unlike atom pair, $S_{ij}(Q)$. A complete structural study of these materials involves the determination of three partial structure factors. In order to determine these partial structure factors, at least three independent diffraction experiments must be carried out so that the weighting factors given by equation 1.5 can be changed independently. The following experimental methods permit us to vary the scattering amplitude f_i without affecting the structure:

- X-ray anomalous dispersion of the scattering amplitude [16-19]: Close to the absorption edge of an element, the scattering amplitude is significantly changed due to resonance effects;
- 2. Isomorphous substitution [20]: One or both elements are partially or totally replaced by physically and chemically similar elements in the specimen;
- 3. Isotopic substitution [21-24]: In neutron diffraction experiments, the scatter-

ing length of an element can be changed by using the appropriate isotopes;

- 4. Polarized neutrons: In ferromagnetic alloys, polarized neutrons will interact with the magnetic moments of the atoms;
- 5. Three radiation experiments [25]: The scattering amplitudes are different for x-ray, neutron, and electron diffraction.

In addition to the above methods, another method which is referred to as the concentration technique has been used to evaluate the partial structure factors for some binary systems. The basic assumption of this method is that the partial structure factors are independent of alloy composition, so that the weighting factors in equation 1.5 can be varied by changing the concentration of the alloying constituents. This method was first used by Halder and Wagner [26] in the study of Ag-Sn alloys. It gives useful information on the partial structure factors for some systems. However, in principle, the partial structure factors are functions of the alloy's composition, and the basic assumption of composition independence of the partial structure factors is not satisfied as will be shown explicitly in this thesis.

The first attempt to separate the partial structure factors of a binary noncrystalline system was made by Enderby *et al.* in 1966 [21] using isotope substitution. Waseda *et al.* then evaluated the partial structure factors of liquid Ni-Si using anomalous x-ray scattering, which was suggested by Ramesh and Ramaseshan in 1971 [19]. O'Leary was the first one to evaluate the partial structure factors of a metallic glass, TbFe₂, using the total structure factors by two different investigators [27]. Since then numerous authors have studied the partial structure factors for a variety of metallic glasses: metal-metalloid (e.g. Fe-B), simple metal-metal (e.g. Mg-Zn), transition metal-transition metal (e.g. Ni-Zr). The experimental methods applied in these previous studies are summerized in Table 1.1.

In principle, three independent experiments allow a complete evaluation of the partial structure factors for a binary system. However, a reliable evaluation of the partial structure factors depends on, the reliability of the original total structure factors, and the contrast among the total structure factor measurements.

Accurate evaluation of the total structure factors is the first step in obtaining reliable partial structure factors. In the last two decades, total structure factors have been studied for numerous amorphous materials. While we may not know the true structure factor of the material, we do know that the experimental structures factors are suspicious if there are considerable differences between various experimental determinations on the same material. In 1982, K. Dint et al. [46] made a comparison of the previous structural studies on Fe-B metallic glasses. They found significant disagreement between two independent but nominally similar xray diffraction measurements: the general form of the two x-ray total structure factor curves was different. These differences in the structure factors which arose due to the errors and uncertainties in the experimental methods and data analysis, were shown to have considerable effects in the subsequent structural determinations. It was suggested that these disagreements in the structure factors were hindering a more complete understanding of the properties of metallic glasses. Unfortunately, their comments did not receive too much attention. Later studies on similar systems seem to totally ignore the previous discussion on the reliability of the experimental data and no further systematic structural study on Fe-B metallic glasses has been reported. In 1989, a careful survey made in reference [47] again reveals significant discrepancies in the total structure factors (as much as 30% at low Q) obtained from independent studies on the same system. Since most of the authors do not display

 Table 1.1: Partial structure factor studies of metallic glasses.

Alloy	Method	Reference
TbFe ₂	Nuclear and magnetic neutron diffraction of $TbFe_2 + x$ -ray diffraction of $GdFe_2$.	[27] (1975)
Ni75Si25	X-ray anomalous scattering using Mo-, Cu-, and Co-K α radiation.	[17] (1976)
$Co_{81}P_{19}$	X-ray nuclear and magnetic neutron scattering.	[28] (1976)
Cu57Zr43	Neutron isotope substitution using the isotopes of Cu.	[29] (1978)
Cu35Ti65	X-ray and neutron diffraction assuming the number- concentration correlation to be negligible.	[30] (1980)
$Ni_x B_{100-x}$	$x = 82 \& 64$, x-ray and neutron diffraction assuming $S_{BB} \sim 0$.	[31] (1981)
$\mathrm{La_{80}Ga_{20}}$	X-ray isomorphous substitution with Al assuming S_{GaGa} to be negligible.	[32] (1981)
Ni60Nb40	X-ray diffraction and neutron diffraction using nat.Ni and ⁵⁸ Ni.	[33] (1981)
Ni35Ti85	X-ray and neutron scattering assuming the number- concentration correlation $=$ hard sphere calculation.	[34] (1982)
*Ni35Zr65	Isomorphous substitution of Zr by Hf in x-ray diffraction and Ni by Co in neutron diffraction.	[35] (1984)
Ni₄0Ti60	Neutron isotope substitution using nat.Ni, ⁵⁸ Ni, and ⁶⁰ Ni.	[36] (1984)
Fe24Zr76	Variation of the Fe composition + isomorphous substi- tution cf Zr with Hf.	[37] (1985)
Ni33Y67	Neutron isotope substitution using nat.Ni, ⁵⁸ Ni, and ⁶⁰ Ni.	[38] (1985)
Be _{37.5} Ti _{62.5}	X-ray and neutron diffraction assuming the number- concentration correlation $=$ hard sphere calculation.	[39] (1985)
Be43Zr57	Isomorphous substitution with 5, 25, 54% of Hf.	[40] (1986)
Ti84Si16	X-ray and neutron diffraction assuming $S_{SiSi} = 0$.	[41] (1986)
C025 Ti75	X-ray and neutron diffraction assuming the number- concentration correlation to be negligible.	[42] (1987)
Cu ₃₃ Zr ₆₇	X-ray anomalous scattering (synchrotron source).	[43] (1988)
Mg70Zn30	X-ray anomalous scattering using W-L α_1 , Au-L α_2 , and Mo-K α_1	[44] (1991)
Ni44 Nb56	TOF neutron scattering using ⁵⁸ Ni, ⁶⁰ Ni, and ⁰ Ni.	[45] (1992)

* Recent structural studies on Ni-Zr amorphous alloys are summerized in Table 1.2.

Chapter 1. Introduction

either the experimental raw data, or give the details of their data reduction, it is rather difficult to trace the origin of these large discrepancies. However, one can certainly conclude that the uncertainties in these total structure factors are about the level of these discrepancies.

As discussed in reference [48], in determining partial structure factors, the errors in the total structure factors can be greatly amplified when there is little contrast among the measurements. Unfortunately, the changes in the weighting factors, w_{ij} , by any of the methods listed on page 5 are usually relatively small. For neutron scattering, some favorable cases exist when one of the alloying elements has an isotope of negative scattering length (e.g. ⁷Li, ^{nat.}Ti, ^{nat.}Mn, and ⁶²Ni). But this isotope-enrichment technique is not an easy method and at the present time the cost of isotopes is usually prohibitive. Therefore, the low contrast of weighting factors is a major problem in the determination of reliable partial structure factors. In addition to the errors which are propagated from the total structure factors, large uncertainties may arise from the various approximations which are made during the data reduction. For example, when the changes in the weighting factors are too small to yield physically meaningful functions, frequently, only two of the partial structure factors are approximately determined (see Table 1.1). There is usually no direct evidence to support these assumptions, and the uncertainties due to these approximations are not discussed. In many cases, if three of the partial structure factors were derived, the evaluation procedures are not discussed even though the three linear equations are obviously ill-conditioned.

As a consequence, large discrepancies are found among the studies on the same system by different authors. For example, as shown in Table 1.2, many structural studies have been made on amorphous Ni-Zr alloys by different investigators [35,49-

$Ni_x Zr_{100-x}$	Ni-Ni		Ni-Zr		Zr-Ni		Zr-Zr		<u></u>	
x	r (Å)	Ν	r (Å)	N	r (Å)	Ν	r (Å)	Ν	Reference	
24.1			2.70	14.5	2.70	4.6	3.16	8.4	[49]	
24.1			2.62	2.35	2.62	0.84	3.17	9.66	[50]	
25.0		< 1.3	2.76	12.6	2.76	4.2	3.23	11.0	[51]	
25.0	2.63	1.8	2.66	8.6	2.66	2.8	3.16	10.9	[52]	
			0 70	~ ~	0.70			10.0	[10]	
33.3			2.70	8.3	2.70	4.2	3.16	10.6	[49]	
33.3			2.62	2.39	2.62	1.43	3.18	10.1	[50]	
			~ ~~	- .					(a -1)	
35.0	2.66	2.3	2.69	5.4	2.69	2.9	3.15	9.0	[35]	
35.0	2.66	2.3	2.69	7.9	2.69	4.3	3.15	9.1	[53]	
36.0	2.45	3.3	2.85	8.56	2.85	4.81	3.30	11.0	[54]	
00.0		••••					0.00		[0]]	
36.5			2.70	9.6	2.70	5.6	3.16	8.6	[49]	
36.5			2.62	2.44	2.63	1.56	3.20	8.91	[50]	
50.0	2.63	3.3	2.73	6.7			3.32	7.8	[55]	
									••	
63.7	2.52	6.0	2.67	5.0			3.28	5.8	[56]	
63.7	2.63	6.4	2.70	5.3			3.28	6.6	[57]*	
64.0	2.52	6.0	2.66	5.0			3.26	5.0	[58]	

Table 1.2: Interatomic distances and partial coordination numbers of melt-spun Ni-Zr glasses.

* Reference [57] is entitled "Anomalous wide angle z-ray scattering of amorphous Ni_2Zr alloy", but in the text it said that the sample was a piece of ribbon used in reference [56] which is $Ni_{63,7}Zr_{36,3}$.

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53,55], but the results for the most important structural parameters such as the interatomic distances and the coordination numbers ². are inconsistent. The same situation is also found in the studies of other amorphous alloys [48,59]. These conflicting results can be misleading to theoretical modeling and the calculations of various properties of these materials.

As a matter of fact, when the partial structure factors of a non-crystalline system were evaluated for the first time, J. E. Enderby *et al.* [21] found that, in addition to the three neutron diffraction measurements with isotope substitutions, a fourth measurement using x-ray diffraction was most valuable because it provided necessary constraints to the ill-conditioned linear equations from the neutron diffraction experiments. They concluded that although theoretically only three scattering measurements are required, the difficulties of calibration and the general uncertainties with the total structure factors make it important that the weighting factors of the different measurements be widely spaced ³; otherwise at least four experiments are required. Indeed, since the low contrast among the measurements means lack of information, the only solution is to make systematic and mathematically redundant measurements. Unfortunately, this critical advice has not been widely followed. As a consequence, large uncertainties and discrepancies are found in experimentally determined structure factors.

Strongly motivated by the above discussion, a careful and comprehensive structural study on Ni-Zr metallic glasses is reported in this work. The amorphous Ni-Zr

²These structural parameters are evaluated from the partial atomic distribution functions, which are the Fourier transforms of the corresponding partial structure factors (See chapter 2 for the details). Extended x-ray absorption fine structure can also provide this structural information.

³Note that in their work, the scattering length was changed by about 60%, while that of many later studies is only 10-20%

system was chosen for this research for the following reasons:

- 1. An assortment of experimental methods are available for evaluating the partial structure factors of this particular system, they are:
 - Zr has an ideal isomorphous substituent, Hf. Previous studies on various properties of Ni-Zr and Ni-Hf alloys indicate that Hf is very physically and chemically similar to Zr [60,61]. Therefore, partially or totally replacing Zr by Hf will probably change the scattering amplitude without affecting the structure of the alloy;
 - Ni has several isotops and one of them has a negative neutron scattering length. Different combinations of the Ni isotopes can be used to vary the neutron scattering amplitudes with no change to the structure. One can even obtain one of the partial structure factors directly from a single experiment with the zero alloy⁴.
 - The anomalous scattering method can be applied at the K-absorption edges of both Ni and Zr, especially, at the k-edge of Zr, the scattering length changes about 20% and the maximum value of Q can be as high as 16 $Å^{-1}$.
- 2. Ni-Zr is an easy glass forming system, therefore, studies of the electron transport properties [62,63], the variation of the superconducting transition temperature [63,64], magnetic susceptibility [63,65], and the crystallization temperature [66-69] have been carried out systematically. Interpretation of these

⁴With an isotope which has a negative scattering length, zero scattering length can result from appropriate combination of the isotopes so that two of the three weighting factors become zero. Such a alloy made especially for a neutron diffraction experiment is called *a zero alloy*.

experimental results would be greatly aided by an accurate knowledge of the partial structure factors.

- 3. Theoretical modeling of the amorphous Ni-Zr system has made substantial progress in recent years [70-73]. Comparison between the models and experiment plays an important role in improving these models, and therefore, accurate and systematic experimental studies of the structure of amorphous Ni-Zr alloys are required.
- 4. Several structural studies have been done on amorphous Ni-Zr alloys since 1982. However, as shown in Table 1.2, large discrepancies exist among the results obtained by different authors. Further experimental study is required to clarify the confusion in the previous studies and complete our understanding of the structure of this system.
- 5. Amorphous Ni-Zr alloys can be produced in a wide composition range, from Ni₈₀Zr₂₀ to Ni₂₀Zr₈₀. However, as Table 1.2 shows, the structural studies have concentrated only on the Zr-rich alloys. It has been found that various other properties of these materials are composition dependent. Therefore, it is of interest to study the structure factors as a function of composition;

This thesis presents the results of a careful and systematic structural study on the amorphous Ni-Zr system. It aims to improve our understanding of the structure of these important metallic glasses and clarify the confusion in the previous studies. Amorphous ribbons of $Ni_x(Zr_yHf_{1-y})_{1-x}$, x = 0.3, 0.33, 0.4, 0.45, 0.5, 0.6, 0.67 and y = 1, 0.9, 0.8, 0.6, 0.3, 0.15 0.0, were prepared using the melt-spinning technique. Amorphous films of Ni_xZr_{1-x} , x = 0.31, 0.36, 0.46, 0.53, 0.66, 0.75, 0.86, were prepared using the DC magnetron sputtering technique. X-ray and neutron diffraction experiments were performed to obtain the total structure factors. A comparison between the structures of melt-spun and sputtered Ni-Zr glasses is made in terms of the structure factor, S(Q), and the atomic pair distribution function, g(r), over a wide range of composition. The partial structure factors of amorphous Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} are evaluated, and the reliability of these partial structure factors is discussed. The compositional dependence of the Faber-Ziman partial structure factors is then examined. The chemical short range order in amorphous Ni-Zr alloys is discussed in terms of the Bhatia-Thornton partial structure factors.

A feasibility study using anomalous x-ray scattering was undertaken. The results were somewhat disappointing. However refinement of our measuring technique as described in Appendix B would make this a useful tool for partial structure factor determination.

Chapter 2 Theoretical background

In non-crystalline materials, there is no overall regularity, such as the lattice structure found in crystalline solids. Instead, the atoms are randomly positioned in space. Their microstructure can therefore be described with a one-dimensional probability function, the atomic pair distribution function, g(r). One can not directly observe the real space structure of these materials, but the Fourier transform of the atomic pair distribution function, the structure factor, can be obtained from diffraction experiments. In this chapter, the relation between diffraction data and the distribution function is briefly described. Detailed descriptions can be found in the literature [7-10].

2.1 Description of the structure of non-crystalline systems

For a system with an average number density $\rho_o = N/V$, the atomic pair distribution function is defined as [6]

$$g(r) = \frac{\rho(r)}{\rho_o} \tag{2.1}$$

where $\rho(r)$ is the local atomic number density. Because the position correlation of atoms weakens with increasing distance, $\rho(r)$ gradually approaches the average number density ρ_o at large values of r. This characteristic means that

$$\lim_{t \to \infty} g(r) = 1 \tag{2.2}$$

On the other hand, due to the repulsion in the pair potential, the atoms do not mutually approach within the atomic core diameter. Therefore,

$$\lim_{r \to 0} g(r) = 0 \tag{2.3}$$

Basically, the atomic pair distribution function g(r) shows the deviation from the average number density ρ_o .

The information given by g(r) is only one-dimensional, but it does give quantitative information about the non-crystalline system. For a multi-component system, the relatively low information content of g(r) can be considerably enchanced if the partial distribution functions, $g_{ij}(r)$, where i and j index the various types of atoms, can be obtained.

Instead of the pair distribution function g(r), another function called the "radial distribution function" (RDF) is also frequently used in the discussion of noncrystalline materials. The RDF(r) is defined as:

$$RDF(r) = 4\pi r^2 \rho_o g(r) \tag{2.4}$$

It corresponds to the number of atoms in the spherical shell between r and r + dr. As the pair distribution function approaches unity at large value of r, the radial distribution function becomes close to the parabolic function $4\pi r^2 \rho_o$. Figure 1.1 shows schematic diagrams for g(r) and RDF(r). By definition, the average number



Figure 2.1: Schematic diagram of the atomic pair distribution function g(r) and the radial distribution function RDF(r).

of atoms in a shell between r_1 and r_2 can be estimated from the area under the radial distribution function in the region between r_1 and r_2 :

$$N = \int_{r_1}^{r_2} 4\pi r^2 \rho_o g(r) dr = \int_{r_1}^{r_2} RDF(r) dr \qquad (2.5)$$

N is called the "coordination number". In particular, the coordination number of nearest-neighbor atoms, N_1 , can be obtained from the area under the first peak of RDF. The quantity N_1 has been frequently used to characterize a non-crystalline system.

2.2 Relations between the distribution function and the diffraction experiments

X-rays, neutrons, and electrons have been widely used to determine the structure of matter. In particular, x-ray diffraction is the most popular and the most important method in the structural analysis of crystalline and non-crystalline materials. An xray diffractometer is like a Fourier transform device. It records the Fourier spectrum of the real space distribution of the atoms in the material as will now be shown.

Consider a system of randomly positioned atoms, let r_k represent the instantaneous position of atom k, Q_o and Q' represent the incident and scattered x-rays ¹, the coherent scattering intensity in electron units is then given by

$$I_{coh}(\mathbf{Q}) = \sum_{j} f_{j}(\mathbf{Q}) e^{-i(\mathbf{Q}'-\mathbf{Q}_{0})\mathbf{r}_{j}} \sum_{k} f_{k}(\mathbf{Q}) e^{-i(\mathbf{Q}'-\mathbf{Q}_{0})\mathbf{r}_{k}} = \sum_{j} \sum_{k} f_{j}(\mathbf{Q}) f_{k}(\mathbf{Q}) e^{-i\mathbf{Q}(\mathbf{r}_{j}-\mathbf{r}_{k})}$$
(2.6)

Define the angle between the vectors Q_o and Q' as $2\theta^2$ and let $Q = Q' - Q_o$, one obtains the relation

¹The discussion also applies to both thermal neutrons and electrons.

²2 θ is usually called the scattering angle.

$$Q = |\mathbf{Q}' - \mathbf{Q}_o| = \frac{4\pi}{\lambda} \sin\theta \tag{2.7}$$

where λ is the wavelength of the x-rays. Since each vector $\mathbf{r}_{jk} = \mathbf{r}_j - \mathbf{r}_k$ takes all orientations, the average for each exponential term in equation 2.6 is given by

$$\langle e^{-i\mathbf{Qr}_{jk}} \rangle = \frac{1}{4\pi r_{jk}^2} \int_{\phi=o}^{\pi} e^{-i\mathbf{Qr}_{jk}\cos\phi} 2\pi r_{jk}^2 \sin\phi d\phi = \frac{\sin\mathbf{Qr}_{jk}}{\mathbf{Qr}_{jk}}$$
 (2.8)

Thus one can re-write the coherent scattering intensity in the form

$$I_{coh}(Q) = \sum_{j} \sum_{k} f_j(Q) f_k(Q) \frac{\sin Q r_{jk}}{Q r_{jk}}$$
(2.9)

Equation 2.9 is often called the "Debye scattering equation" [9,74].

2.2.1 One-component systems

For a one-component system of N atoms, the Debye scattering equation reduces to the form

$$I_{coh}(Q) = f^2(Q) \sum_j \sum_k \frac{sinQr_{jk}}{Qr_{jk}}$$

$$(2.10)$$

Since in performing the summation of equation 2.10 each atom in turn becomes the origin atom, there are then N terms due to the interaction of each atom with itself. Hence equation 2.10 may be written

$$I_{coh}(Q) = Nf^{2}(Q)(1 + \sum_{j \neq k} \frac{sinQr_{jk}}{Qr_{jk}})$$
(2.11)

As discussed in the preceding section, the probability of finding another atom at a distance r from an origin atom is expressed by the function $\rho(r)$. Using this function the distribution of atoms about any reference atom may now be regarded as a continuous function, and hence the summation can be replaced by an integral

$$I_{coh}(Q) = N f^{2}(Q) [1 + \int_{o}^{\infty} 4\pi r^{2} \rho(r) \frac{\sin Qr}{Qr} dr]$$
(2.12)

According to equation 2.1,

$$\rho(r) = \rho_o g(r) \tag{2.13}$$

where g(r) is the atomic pair distribution function. Since for large values of r, $g(r) \rightarrow 1$, one can re-write the above equation in the form

$$\rho(r) = \rho_o[g(r) - 1] + \rho_0 \tag{2.14}$$

Substitute equation 2.14 into equation 2.12,

$$I_{coh}(Q) = Nf^{2}(Q)\{1 + \int_{o}^{\infty} 4\pi r^{2}\rho_{o}[g(r) - 1]\frac{sinQr}{Qr}dr + \int_{0}^{\infty} 4\pi r^{2}\rho_{o}\frac{sinQr}{Qr}dr\}$$
(2.15)

The second integral of equation 2.15 is the central scattering, which has physical significance only at extremely small angles. This term is frequently neglected in practical calculations.

Let $I^a_{coh}(Q)$ represents the coherent scattering intensity per atom:

$$I^a_{coh}(Q) = \frac{I_{coh}(Q)}{N}$$
(2.16)

The "structure factor", S(Q), is defined as [75]

$$S(Q) = \frac{I_{coh}^{a}(Q)}{f^{2}(Q)}$$
(2.17)

Following equations 2.15 and 2.16, the structure factor is related to the atomic pair distribution function by

$$S(Q) = 1 + \int_{o}^{\infty} 4\pi r^{2} \rho_{o}[g(r) - 1] \frac{\sin Qr}{Qr} dr$$
(2.18)

By means of the Fourier integral theorem, this expression can be transformed to

$$\tau \rho_0[g(r) - 1] = \frac{1}{2\pi^2} \int_0^\infty Q[S(Q) - 1] sinQrdQ$$
 (2.19)

or

$$RDF(r) = 4\pi r^{2} \rho(r) = 4\pi r^{2} \rho_{o} + \frac{2r}{\pi} \int_{o}^{\infty} Q[S(Q) - 1] sinQrdQ \qquad (2.20)$$

In summary, equations 2.15 to 2.20 reveal the fact that the experimental intensity $I_{coh}(Q)$ is indeed the Fourier transform of the atomic distribution function g(r).

2.2.2 Multi-component systems

For a n-component system, the structure factor derived from a diffraction experiment is composed of $\frac{1}{2}n(n+1)$ partial structure factors. The partial structure factors are commonly defined using three different formalisms [11-13]. The essential features of these different partial structure factors and the relations between them are summerized below.

The Ashcroft-Langreth particl structure factors

In 1967, Ashcroft and Langreth [11] proposed the following definition for the partial structure factors of a multi-component non-crystalline system:

$$S_{jk}(Q) = (N_j N_k)^{-1/2} < \sum_j \sum_k e^{-i\mathbf{Q}(\mathbf{r}_j - \mathbf{r}_k)} > -(N_j N_k)^{-1/2} \delta_{\mathbf{Q},0}$$
(2.21)

In this definition, the central scattering is excluded. Combining equation 2.6 with equation 2.21, the coherent scattering per atom can be expressed as

$$I_{coh}^{a}(Q) = \sum_{j} \sum_{k} (c_{j}c_{k})^{1/2} f_{j}(Q) f_{k}(Q) S_{jk}(Q)$$
(2.22)

at large value of Q, the atoms independently scatter x-rays, therefore,

$$\lim_{Q \to \infty} I^{a}_{coh}(Q) = \frac{1}{N} \sum_{j} f^{2}_{j}(Q) = \langle f^{2}(Q) \rangle$$
(2.23)

and

$$\lim_{Q \to \infty} S_{jk}(Q) = \delta_{jk} \tag{2.24}$$

Thus the Ashcroft-Langreth total structure factor is given by

$$S(Q) = \frac{I_a^{coh}(Q)}{N < f^2(Q) >} = \sum_j \sum_k (c_j c_k)^{1/2} \frac{f_j(Q) f_k(Q)}{< f^2(Q) >} S_{jk}(Q)$$
(2.25)

The number-density function $\rho_{jk}(r)$ is introduced to express the number of j-type atoms found at a radial distance r from a k-type atom:

$$\rho_{jk}(r) = c_k \rho_o g_{jk}(r) \tag{2.26}$$

where $g_{jk}(r)$ is the partial atomic pair distribution function. $g_{jk}(r)$ is related to the partial structure factor $S_{jk}(Q)$ as follows:

$$S_{jk}(Q) = \delta_{jk} + (c_j c_k)^{1/2} \rho_o \int_o^\infty [g_{jk}(r) - 1] e^{-i\mathbf{Q}\mathbf{r}} dr \qquad (2.27)$$

The Faber-Ziman partial structure factors

In their work on the electron transport properties of liquid binary alloys, Faber and Ziman used a different expression for the partial structure factors [12]:

$$I^{a}_{coh}(Q) = \langle f^{2}(Q) \rangle - \langle f(Q) \rangle^{2} + \sum_{j} \sum_{k} c_{j} c_{k} f_{j}(Q) f_{k}(Q) S_{jk}(Q)$$
(2.28)

where, for a binary system

$$\langle f^{2}(Q) \rangle = c_{1}f_{1}^{2}(Q) + c_{2}f_{2}^{2}(Q)$$
 (2.29)

$$\langle f(Q) \rangle = c_1 f_1(Q) + c_2 f_2(Q)$$
 (2.30)

The term $\{\langle f^2(Q) \rangle - \langle f(Q) \rangle^2\}$ is called the Laue monotonic scattering term. $I^a_{coh}(Q)$ approaches $\langle f^2(Q) \rangle$ as $Q \to \infty$, therefore,

$$\lim_{Q \to \infty} S_{jk}(Q) = 1 \tag{2.31}$$

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The Faber-Ziman total structure factor is then given by

$$S(Q) = \frac{I_{coh}^{a}(Q) - (\langle f^{2}(Q) \rangle - \langle f(Q) \rangle^{2})}{\langle f(Q) \rangle^{2}}$$
(2.32)

$$= \sum_{j} \sum_{k} \frac{c_{j} c_{k} f_{j}(Q) f_{k}(Q)}{\langle f(Q) \rangle^{2}} S_{jk}(Q)$$
(2.33)

By this definition the total structure factor is normalized to unity at large value of Q.

The Faber-Ziman partial structure factors are related to the corresponding partial pair distribution function by the following:

$$S_{jk}(Q) = 1 + \rho_o \int [g_{jk}(r) - 1] e^{-i\mathbf{Q}\mathbf{r}} d\mathbf{r}$$
 (2.34)

and

$$4\pi r \rho_o[g_{jk}(r) - 1] = \frac{2}{\pi} \int Q[S_{jk}(Q) - 1] sin(Qr) dQ \qquad (2.35)$$

Bhatia-Thornton partial structure factors

In Bhatia-Thornton formalism, the total coherent scattering intensity per atom is expressed by

$$I_{a}^{coh}(Q) = \langle f(Q) \rangle^{2} S_{nn}(Q) + (\Delta f(Q))^{2} S_{cc}(Q) + 2 \langle f(Q) \rangle \Delta f(Q) S_{nc}(Q)$$
(2.36)

where $S_{nn}(Q)$, the number-number partial structure factor, represents the number density fluctuation; $S_{cc}(Q)$, the concentration-concentration partial structure factor, expresses the concentration fluctuation; and the $S_{nc}(Q)$, the number-concentration partial structure factor, gives the correlation between the number density and concentration³. From 2.36 the Bhatia-Thornton total structure factor is obtained:

³The Bhatia-Thornton partial structure factors were original derived from the Fourier transform of the local number density and concentration fluctuations. In the long wavelength limit the Bhatia-Thornton partial structure factors directly relate to the thermodynamic porperties of a binary alloy. Waseda has given extensive discussion on Bhatia-Thornton partial structure factors and their applications in the study of amorphous materials [76].

$$S(Q) = \frac{I_a^{coh}(Q)}{\langle f^2(Q) \rangle}$$
 (2.37)

$$= \frac{\langle f(Q) \rangle^2}{\langle f^2(Q) \rangle} S_{NN}(Q) + \frac{(\Delta f(Q))^2}{\langle f^2(Q) \rangle} S_{CC}(Q) + \frac{2 \langle f(Q) \rangle \Delta f(Q)}{\langle f^2(Q) \rangle} S_{NC}(Q)$$
(2.38)

and

$$\lim_{Q \to \infty} S(Q) = 1 \tag{2.39}$$

Equations 2.38 and 2.39 suggest the following relations:

$$\lim_{Q \to \infty} S_{NN}(Q) = 1 \tag{2.40}$$

$$\lim_{Q \to \infty} S_{CC}(Q) = c_1 c_2 \tag{2.41}$$

$$\lim_{Q\to\infty}S_{NC}(Q) = 0 \tag{2.42}$$

The Fourier transform of the Bhatia-Thornton partial structure factors give the corresponding pair correlation functions:

The number-number pair correlation function $\rho_{nn}(r)$

$$4\pi r[\rho_{nn}(r) - \rho_o] = \frac{2}{\pi} \int_o^\infty Q[S_{NN}(Q) - 1] sinQrdQ$$
(2.43)

The concentration-concentration pair correlation function $ho_{cc}(r)$

$$4\pi r \rho_{cc}(r) = \frac{2}{\pi} \int_{0}^{\infty} Q[S_{CC}(Q) - c_1 c_2] sinQrdQ \qquad (2.44)$$

The number-concentration pair correlation function $\rho_{nc}(r)$

$$4\pi \tau \rho_{nc}(r) = \frac{2}{\pi} \int_{o}^{\infty} Q S_{NC}(Q) \sin Q r dQ \qquad (2.45)$$

The correlation function $\rho_{nn}(r)$ describes the topological short-range order of the system. The concentration correlation function, $\rho_{cc}(r)$ characterizes the composition (or chemical) short-range order. The quantity $\rho_{nc}(r)$ expresses the correlation between density and concentration fluctuation.
The three sets of partial structure factors can be mutually transformed by linear relations. Each of them may be found superior to the other two under certain circumstances. In principle, both the Ashcroft-Langreth and Faber-Ziman partial structure factors are functions of the atomic concentration. However, the Ashcroft-Langreth formalism is more sensitive to the composition of the system than the Faber-Ziman formalism because the latter does not explicitly involve the composition [6]. In some cases, the Bhatia-Thornton partial structure factors are particularly interesting not only because they directly relate to the thermodynamic properties of the material, but also because there are several practical advantages in using these partial structure factors in experimental studies. For example, in a neutron diffraction experiment, if one of the constituent atoms has an isotope of negative scattering length, the average scattering length of the alloy can be made zero by appropriate isotop-enrichment. Such an alloy is called a "zero alloy". According to equation 2.38, the partial structure factor $S_{cc}(Q)$ of a zero alloy is directly obtained from normalizing the coherent scattering intensity as:

$$S_{cc}(Q) = \frac{S(Q)}{(\Delta b)^2 / \langle b^2 \rangle} = \frac{I_{coh}(Q)}{(\Delta b)^2}$$
(2.46)

In this thesis, only Faber-Ziman and Bhatia-Thornton partial structure factors are used. The linear transformation between these two sets are given below:

$$S_{NN}(Q) = c_1^2 S_{11}(Q) + c_2^2 S_{22}(Q) + 2(c_1 c_2) S_{12}(Q)$$
(2.47)

$$S_{CC}(Q) = c_1 c_2 [1 + c_1 c_2 (S_{11}(Q) + S_{22}(Q) - 2S_{12}(Q))]$$
(2.48)

$$S_{NC}(Q) = c_1 c_2 [c_1 (S_{11}(Q) - S_{12}(Q)) - c_2 (S_{22}(Q) - S_{12}(Q))]$$
(2.49)

2.3 The chemical short-range order in metallic glasses

Since most metallic glasses are alloys, the state of mixing of the alloy components is an important parameter characterizing the system. In most cases, a completely random mixture is not attained, therefore, the chemical composition around each type of atoms differs from the average composition. There then exists chemical short-range order (CSRO) in the system. The CSRO as a function of radial distance is best described with the composition fluctuation atomic pair correlation function $\rho_{cc}(r)$, which can be obtained from the Fourier transform of the Bhatia-Thornton concentration-concentration structure factor $S_{cc}(Q)$ (see equ. 2.44).

The probability of finding an atom of any type at distance r from j-atom can be expressed by

$$\rho_j(r) = \rho_{j1}(r) + \rho_{j2}(r) \tag{2.50}$$

where j = 1 and 2. In terms of $\rho_{12}(r)$ and $\rho_j(r)$, $\rho_{cc}(r)$ can be expressed explicitly by

$$\rho_{cc}(r) = c_2 \rho_1(r) + c_1 \rho_2(r) - \frac{\rho_{12}(r)}{c_2}$$
(2.51)

The generalized Warren-Cowly chemical short-range order parameter ⁴, $\alpha(r)$ is defined as [14,15]

$$\alpha(r) = 1 - \frac{\rho_{12}(r)}{c_2[c_2\rho_1(r) + c_1\rho_2(r)]}$$
(2.52)

Equation 2.51 can be then reduced to

$$\rho_{cc}(r) = [c_2 \rho_1(r) + c_1 \rho_2(r)] \alpha(r)$$
(2.53)

⁴The Warren chemical short-range order parameter was originally proposed for crystalline substitutional solid solutions [9]. This parameter has been widely extended to describe the local chemical short-range order in disorder materials.

For a completely random mixture, $\rho_1(r) = \rho_2(r) = \rho_o$ and $\rho_{12}(r) = c_2\rho_o$, so that $\alpha(r) = 0$ and therefore, $\rho_{cc}(r) = 0$.

The quantity $\rho_{12}(r)$ represents the probability of finding an unlike atom from the origin atom, while the term $\{c_2\rho_1(r) + c_1\rho_2(r)\}$ represents that of finding any type of atom at distance r. Therefore, when $\alpha(r) < 0$, or

$$c_2\rho_1(r) + c_1\rho_2(r) < \frac{\rho_{12}(r)}{c_2}$$
 (2.54)

there exists a preference of unlike atoms, which means that short-range chemical ordering exists in the system. On the other hand, $\alpha(r) > 0$ is an indication of like atoms clustering in the system. Note that the sign of $\rho_{cc}(r)$ goes with that of $\alpha(r)$. $\rho_{cc}(r)$ modulates about zero; the minima (negative peaks) correspond to the distances with preferred unlike atom pairs, whereas maxima (positive peaks) indicate preference for like atom pairs.

In many cases, only the first peak in $\rho_{cc}(r)$ is well defined. Therefore, $\alpha(r)$ is frequently reduced to the parameter:

$$\alpha_1 = 1 - \frac{N_{12}}{c_2(c_2N_1 + c_1N_2)} \tag{2.55}$$

where, following equations 2.5 and 2.35,

$$N_{12} = \int_{r_1}^{r_2} 4\pi r^2 \rho_{12}(r) dr \qquad (2.56)$$

and

$$N_j = N_{j1} + N_{j2} \tag{2.57}$$

with j = 1 or 2.

It should be noted that Cargill *et al.* proposed another criterion to characterize the chemical short-range order in amorphous alloys [77]. It has been shown previously [78] that, to a first approximation, the chemical short-range order coefficient η_{jk} defined by Cargill and Spaepen is equal but opposite in sign to the parameter α_1 .

In this work, the quantity $\alpha(r)$ and the parameter α_1 are used in the discussion of the chemical short-range order in metallic glasses.

Chapter 3 Experimental Methods

3.1 Sample preparation

Amorphous alloys can be made using a variety of techniques. the method of meltspinning has been widely used to produce amorphous ribbons. The narrow ribbons (about 2mm wide) prepared in this work are convenient for electric transport measurements and neutron diffraction ¹; but are not as convenient for x-ray diffraction measurements which require a large flat-surface area. Thin plates of amorphous alloys can be made using magnetron sputtering and they are ideal for x-ray diffraction experiments. In this work, the Ni-Zr glasses are prepared using both melt-spinning and RF magnetron sputtering. For Ni-Zr-Hf alloys, only melt-spun ribbons were prepared because it is difficult to control the composition of a ternary alloy during the sputtering. The composition of the melt-spun ribbons and sputtered films were examined using an electron microprobe.

3.1.1 Melt-spun amorphous ribbons

Amorphous $Ni_x(Zr_yHf_{1-y})_{1-x}$ (x = 0.67, 0.64, 0.60, 0.50, 0.40, 0.33 and 0.30; y = 1.0, 0.9, 0.8, 0.6, 0.3, 0.15) were prepared and characterized as described below.

¹A cylinder can be made of tightly packed ribbons

Small ingots of approximately 1 gram were prepared by arc melting appropriate amounts of Ni (99.99% pure), 7: (99.95% pure), and Hf (99.99% pure) under titanium-gettered argon. Each ingot was melted up to six times to ensure homogeneity. The weight loss due to the melting was found to be less than 1%. The amorphous Ni-Zr anf Ni-Zr-Hf ribbons were prepared in a helium atmosphere using the single roller melt spinning technique. Details of this procedure can be found in references [66,79].

Figure 3.1 is a schematic diagram of the melt-spinning apparatus. A few small ingots totalling 2 to 3 grams were used for each spin. The voltage applied to the motor which drives the spinning wheel was about 20 volts, corresponding to a tangential wheel speed of about 30 m/sec. The quartz crucible used in this work has a relatively large nozzle, diameter ≥ 0.7 mm. The crucible can be cleaned with HF acid and reused. The ribbons were about 2 mm wide, 30 μm thick, and a few meters long. The composition of the ribbons was measured using an electron microprobe. The composition of the ribbons was the same as that of the ingots.

The as-quenched ribbons were determined to be amorphous by taking x-ray diffraction patterns of each side. Since ribbons of the same composition from different spins may be used together in a diffraction experiment, differential scanning calorimetry (DSC) analysis was conducted to further characterize the ribbons from each spin. The crystallization enthalpy can be used as a measure of the disorder in amorphous materials [68]. A low crystallization enthalpy indicates that some small crystallites may exist in the material, which are not detected by x-ray diffraction. In this work, amorphous Ni-Zr-Hf ribbons with the same composition from different spins were found to have the same crystallization enthalpy (with a deviation of $\leq 5\%$).



Figure 3.1: Schematic diagram of the melt-spinning apparatus.

3.1.2 Sputtering amorphous films

Amorphous Ni-Zr films were prepared by rf sputtering of the targets onto watercooled substrates in a triode sputtering apparatus². To ensure the homogeneity of the sputtered films, alloy targets were used.

The Ni_xZr_{1-x} (x = 0.8, 0.7, 0.6, 0.5, 0.4, 0.3, 0.2) alloy targets were prepared by arc melting appropriate amounts of Ni (99.99% pure) and Zr (99.8% pure) under titanium gettered argon in a copper crucible. The crucible was 38 mm in diameter and 0.5 cm deep. Such an alloy target weighs about 70 grams. Films of the Ni-Zr alloys were then prepared by RF sputtering of alloy targets onto water-cooled substrates. The substrate material was Si(11) with a coating of Pd. The coating was to prevent the Zr from interacting with silicon and is less than 100Åthick, which is too thin to cause any significant contamination to the Ni-Zr film. Figure 3.2 is a schematic diagram of the setup inside the sample chamber. Each deposition was preceded by pumping the sample chamber to a base pressure of $7 - 8 \times 10^{-8}$ Torr before introducing the high-purity argon sputtering gas. Pre-sputtering up to 30 min. before each deposition served to clean the target surface and to getter residual impurities.

The sputtered films were determined to be amorphous using x-ray diffraction and differential scanning calorimetry. The composition of the amorphous Ni-Zr films was analysed using the electron microprobe. Up to five points across the whole area of a film were examined and the composition was found to be uniform over the film. However, it was found that the composition of the films systematically differed from that of the targets. As shown in Table 3.1, the films were nickel rich compared to the target. This is explained by the fact that nickel has a higher sputtering rate

²Details of this procedure can be found in the literature [80].



Figure 3.2: Schematic diagram of the set-up in the RF sputtering sample chamber.

Table 3.1: Composition of the sputtered Ni-Zr amorphous films.

	Composition (Ni-Zr at%)							
target	20-80	30-70	40-60	50-50	60-40	70-30	80-20	
film	31.3-68.7	35.8-64.2	46.0-54.0	53.0-47.0	66.0-34.0	75.3-24.7	86.0-14.0	

than zirconium.

3.1.3 Samples for diffraction experiments

The sputtered amorphous films are ideal for x-ray diffraction experiments. A sample holder, made of aluminum, consists of two blocks with rectangular $(50 \times 15 mm^2)$ openings (see figure 3.3) was used to mount the films.



Figure 3.3: Schematic diagram of the sample holder used in *z*-ray diffraction experiments.

It is more challenging to prepare a flat surface with desired area out of the melt-spun amorphous ribbons. The as-made ribbons were first cut into pieces 5 cm

long. About twenty pieces of these ribbons were arranged parallel to one another and the ends fixed on an aluminum frame using double sided tape. The ribbons slightly overlap one another and hence there are no gaps between the pieces. The homogeneity of these surfaces is examined using the method described in section 3.4.

The neutron diffraction experiments require cylindrical samples. The samples were prepared using bundles of melt spun Ni-Zr ribbons. The ribbons were cut into pieces of \sim 7 cm long. A glass tube 7 mm in diameter was cut to be a bit shorter than the ribbons. The ribbons were then inserted into the tube and the ends were left out at one end of the tube. A long piece (\sim one meter long) of the same kind of ribbon was used to tie up these ends and to wrap the ribbons tightly. The ribbons were gently pulled out of the tube while they were wrapped and thus a solid bundle 7 cm long and \sim 0.7 cm thick was made. The bundles weighed 8 to 10 grams.

3.2 The x-ray diffraction experiments

The conventional x-ray diffractometer used in this research is an automated Nicolet-Stöe L11 powder diffractometer interfaced to an IBM PC. Silver K_{α} radiation was used and the x-ray wavelength was 0.56 Å. A schematic diagram of the apparatus is given in figure 3.4.

The radius of the diffractometer is R = 179mm. The width of the source slit is 1.8mm, corresponding to an incident beam equatorial divergence of $\alpha = 1.8/179 =$ 0.6° (see figure 3.5). The detector slit was 0.2mm and the angular acceptance of the detector was about 0.3°. Soller slits limit the axial divergence of the beam about 3°. At the center of the diffractometer, the beam is about 10mm high. The width



of the beam at the sample is given by (see figure 3.5):

$$W = R \times \frac{\sin\alpha\sin\theta}{\cos\alpha\cos2\theta} \tag{3.1}$$

where 2θ is the scattering angle. The minimum value of 2θ in these experiments was 4°. At this position, the beam at the sample has the maximum width: $W \sim 38mm$. Accordingly, all the x-ray samples were prepared to be 40mm wide with a height of 15mm which is greater than the beam height of 10mm.



Figure 3.5: Schematic diagram of the x-ray beam intersecting with the sample.

The detector-analyzer assembly includes a scintillating crystal, a phototube, and graphite analyser crystal: The angle the analysing crystal makes with the incoming diffracted beam may be adjusted. The scintillating crystal together with the phototube may be easily rotated about the analysing crystal. When the detector slit is set properly, the transmittance of the detector-analyzer assembly is determined by the band-pass function of the analysing crystal. The band-pass function of the graphite crystal used in this research was measured using a high resolution double crystal x-ray diffractometer (see section 4.1.1). A single channel analyzer (SCA) was used to further select the $K\alpha$ radiation in the diffracted beam. The 2θ scanning method, i.e. the conventional diffractometer technique was used to study the structure of amorphous Ni-Zr(Hf) alloys. The software used to control the ω and 2θ goniometers and to count pulses from the single channel analyzer is basically the same as that in reference [47]. A multiple scan procedure was used. Each experiment includes 20 short (45 min.) 2θ scans. For low angles ($4^{\circ} \leq 2\theta \leq$ 60°) stepwidths of 0.2° were used, for high angles ($60^{\circ} \leq 2\theta \leq 130^{\circ}$) stepwidths of 2° were used. The steptimes were adjusted so that the relative counting statistics were the same at each angle. The error due to counting statistics is typically \sim 0.8%. Including the time taken for the goniometers to move from angle to angle, each experiment takes about 15 hours. Under the same experimental conditions, the air scattering was measured with and without the empty sample holder. Since the samples were prepared larger than the beam size, i.e. the opening of the sample holder is larger than the beam size, the air scattering results are the same with and without the sample holder ³.

3.3 Neutron diffraction experiments

The neutron diffraction experiments were performed using the C2 diffractometer on the DUALSPEC beam station of the NRU reactor at AECL Research, Chalk River, Canada. Figure 3.6 shows the experimental arrangement. The incident beam monochromator is a Si single crystal. The reflection plane (511) was chosen to avoid higher harmonic diffraction from the monochromator. The angle that the Si(511)

³In early experiments with Mo- or Ag-target, a "pre-peak" was found at $2\theta \sim 8^{\circ}$. It was discovered later that this peak was caused by some unknown scattering from the right side of the source slit assembly and the left side of the goniometer. Therefore, the later experiments were carried out with a small piece of lead ($\sim 20 \times 20mm^2$) shielding the right side of the source slit assembly, and a large piece of lead ($200 \times 60mm^2$) hanging beside the detector slit assembly.



Figure 3.6: Schematic diagram of the neutron diffractometer.

planes make with the primary beam was adjusted to select neutrons of wavelength 0.9Å. Since the spectrum of the primary beam is a Maxwellian distribution with the maximum at ~ 1.54 Å, the intensity of neutrons having wavelengths shorter than ~ 0.9 Å is too low to be practical. The detector used on the C2 diffractometer is a modern position sensitive detector with 800 independent channels. This detector counts 80° of diffraction angle simultaneously. Unfortunately, the highest 2 θ position is only about 110° because of hardware limitations. The exact position of the detector together with the wavelength of the monochromatized beam were calibrated using the diffraction pattern of a standard nickel rod.

The samples used in this research were bundles of amorphous Ni-Zr ribbons. The 2θ -scanning technique was used and the experiments were performed in a multiple scan manner similar to that for the x-ray diffraction experiments, except that the detector counted for the same amount of time at each 0.1°. For each short scan (~ 4 hours) the position sensitive detector first covered 2θ from 10° to 90° and then from 30° to 110°. The wide overlap range, $30^{\circ} \leq 2\theta \leq 90^{\circ}$, was helpful in joining the two sections of data. At each position the detector counted for about 2 hours, corresponding to an incident beam monitor number of 10^8 neutrons. Up to 9 scans were carried out for each sample. The room temperature measurements were performed in air. Without the sample the air scattering was measured under the same experimental condition. Measurements were also performed at low temperatures with amorphous ribbons in a vanadium can placed at the center of a cryostat. These low temperature experiments were not very successful because of the irregular Bragg reflections from the aluminum walls of the cryostat.

3.4 Thickness measurements

The x-ray samples used in this research are thin foils. The thickness of the x-ray samples is an important parameter in the data reduction, therefore, it must be known accurately. This section describes a method of measuring the thickness and the thickness uniformity of a thin plate using the x-ray diffractometer.

Usually, when the mass, surface area, and the density of a plate are known its average thickness can be evaluated according to:

$$thickness = \frac{mass}{arca \times density}$$
(3.2)

When the absorption coefficient of the sample is known, the uniformity can be evaluated using the x-ray diffractometer. As shown in figure 3.7, with the detector placed at $2\theta = 0^{\circ}$ (an appropriate attenuator must be placed in front of the detector !), the intensity versus ω is measured for the range of ω used in a regular 2θ scan. The intensity for such a scan is given by

$$I(\omega) = I_o exp(-\frac{\mu t}{sin\omega})$$
(3.3)

where I_o is the incident beam intensity, μ and t are, respectively, the linear absorption coefficient and the thickness of the sample. The above equation can be re-written as

$$ln(I) = ln(I_o) - \mu t \frac{1}{\sin\omega}$$
(3.4)

Equation 3.4 reveals that, if the sample has a uniform thickness, a plot of $\ln(I)$ vs. $1/\sin\omega$ should be a straight line, and the slope of this line is equal to $-\mu t$. The primary beam intensity I_o need not be known but must remain constant during the experiments.



Figure 3.7: Schematic diagram of the setup used to determine the uniformity of a flat plate sample.

Since the mass absorption coefficient μ is proportional to λ^3 a monochromatic incident beam is required. When a conventional x-ray diffractometer, without incident beam monochromator, is used a low voltage should be applied to the x-ray tube to reduce the effect of the short wavelength bremsstrahlung tail.

In this work, a molybdenum target x-ray tube was used for the thickness measurements and a Zr-filter 100 μm thick was placed in front of the source slit⁴. The source and detector slits were the same as that in a regular diffraction experiment. The accuracy of the thickness measurement with this experimental setup was tested using a standard Fe filter film $15\mu m$ thick. It resulted in a perfect straight line and the measured thickness was $15 \pm 1\mu m$. The results for all the x-ray samples made of melt-spun ribbons and sputtered films were found to be straight lines. Figure 3.8 shows a typical result for the x-ray sample made of Ni_{0.33}Zr_{0.67} melt-spun ribbons. The straight line indicates the satisfactory uniformity of the thickness. The slope was found to be: $\mu t = 0.416$, therefore, the average thickness of this sample is:

$$t = \frac{\mu t}{\mu} = \frac{0.416}{161.94} = 25.8\mu m \tag{3.5}$$

where $\mu = 161.94$ is the linear absorption coefficient of Ni_{0.33}Zr_{0.67} for Mo-K α x-rays.

Similar experiments were also performed at the F3 beam station of CHESS. The monochromatized beam was used and the outgoing beam was measured by an ion chamber. The results were found to agree with those obtained using the conventional x-ray diffractometer within 1%.

⁴The x-ray diffraction experiments were performed using silver targets, therefore, it would be better to measure the thickness with the silver tube. Unfortunately, the voltage settings of the Nicolet-Stöe diffractometer are 20kV, 30kV, ... etc. 20kV is too low to excite the Ag-K α radiation while with 30kV, the short wavelength tail is too strong and there was no filter available for the silver target.



Figure 3.8: Results of the thickness measurement for the $Ni_{0.33}Zr_{0.67}$ z-ray sample made of melt-spun ribbons.

Chapter 4 Data analysis

As discussed in chapter 2, the experimental structure factor is derived from the coherent scattering intensity, I_{coh} . In general, I_{coh} is not directly accessible from the diffraction experiments. A number of corrections have to be applied to the raw data depending on the radiation and geometry used in the experiment. In this chapter, the reduction of x-ray diffraction, anomalous x-ray scattering, and neutron diffraction data to obtain the total structure factors is described in detail. The procedure for determining the partial structure factors and the partial atomic pair distribution functions is then discussed.

4.1 Determination of the total structure factors4.1.1 Reduction of x-ray diffraction data

The x-ray scattering intensity for amorphous systems is measured in arbitrary units. To obtain the structure factor from the experimental intensity, several corrections must be applied to the raw data. The observed x-ray scattering intensity may be expressed as [16]

$$I_{obs}(2\theta) = NP[AI_{coh}(Q) + A'I_{inc}(Q) + I_{mul}(Q)] + I_{air} + I_b$$

$$\tag{4.1}$$

where:

I _{obe}	-	the observed x-ray intensity in arbitrary units;
Ν	=	the normalization factor;
Р	=	the polarization factor;
$I_{coh}(Q)$	=	the coherent scattering intensity in electron units;
Α	=	the absorption correction for coherent scattering;
$I_{inc}(Q)$	=	the incoherent scattering intensity in electron units;
Α'	=	the absorption correction for incoherent scattering;
$I_{mul}(Q)$	=	the multiple scattering intensity in electron units;
Lair	=	the air scattering intensity;
Iь	=	the background.

As defined by equations 2.28 and 2.33, $I_{coh}(Q)$ can be expressed as

$$I_{coh}(Q) = \langle f(Q)^2 \rangle + (S(Q) - 1) \langle f(Q) \rangle^2$$
(4.2)

where S(Q) is the Faber-Ziman total structure factor. In terms of S(Q), equation 4.1 can be re-written as

$$I_{obs}(2\theta) = NP\{A[< f(Q)^2 > +(S(Q)-1) < f(Q) >^2] + A'I_{inc}(Q) + I_{mul}(Q)\} + I_{air} + I_b$$

$$(4.3)$$

Based on this equation, the Faber-Ziman total structure factor can be derived from the x-ray diffraction intensity. In the following paragraphs the various quantities in equation 4.3 are discussed in detail.

The x-rays generated at the target are not polarized but become polarized after scattering by the sample and the monochromator. The polarization factor depends on how many times the beam is scattered in an experiment. For the diffraction geometry used in this work the beam is scattered once at the sample and again at the analysing crystal, therefore, the polarization factor P is given by [16]

$$P = \frac{1 + \cos(2\theta_M)^2 \cos(2\theta)^2}{2} \tag{4.4}$$

The quantity $2\theta_M$ is the scattering angle of the monochromator.

The absorption factor A in equation 4.3 is given by (see reference [7], page 801 and 360)

$$A = \frac{1 - exp(-2\mu t \sin\theta)}{2\mu t} \tag{4.5}$$

where μ is the linear absorption coefficient and t is the sample thickness. The thickness and the thickness uniformity of all the x-ray samples were measured using the method described in section 3.4.

Due to the fact that Compton scattering modifies the radiation wavelength, the absorption factor for incoherent scattering is slightly different from that for coherent scattering. When the x-ray wavelength is far from the absorption edges, the absorption coefficient μ is proportional to λ^3 . Therefore, the absorption coefficient for the incoherent diffracted beam is

$$\mu' = \left(\frac{\lambda'}{\lambda}\right)^3 \mu \tag{4.6}$$

where λ' is the wavelength of the incoherently scattered beam [74]:

$$\lambda' = \lambda + 0.0486 sin^2\theta \tag{4.7}$$

Thus the quantity A' is given by

$$A' = \frac{1 - exp[-(\mu + \mu')tsin\theta]}{(\mu + \mu')t}$$
(4.8)

The linear absorption coefficient μ of the alloy can be calculated by

$$\mu = d \sum_{i} w_i \mu_m^i \tag{4.9}$$

where *i* is the type of atoms in the sample, d is the density of the alloy, w_i and μ_m^i are, respectively, the weight percentage and the mass-absorption coefficient of *i* type

atom. Experimental values of the density of Ni-Zr amorphous alloys [63] are shown in figure 4.1 and have been used in calculating μ . The values of the density is given by d = (polynominal in graph).

In general the atomic scattering factor, f, can be expressed as

$$f(Q, E) = f_o(Q) + f'(E) + if''(E)$$
(4.10)

where E is the x-ray energy and is related to the wavelength, λ , by

$$E = \frac{hc/e}{\lambda} = \frac{12.399}{\lambda(\dot{A})}(keV)$$
(4.11)

The quantity $f_o(Q)$ is the scattering factor when the x-ray energy is far from any absorption edge in the atom. f' and f'' are, respectively, the real and imaginary part of the dispersion correction.

The atomic scattering factor f_o has been evaluated from the numerical Hartree-Fork wave functions and tabulated as a function of $sin\theta/\lambda$ [9,81]. Cromer et al [82] have also fitted f_o of various elements and ions to the analytic function

$$f_o(\frac{\sin\theta}{\lambda}) = \sum_{i=1}^{4} a_i exp[-b_i \frac{\sin^2\theta}{\lambda^2}] + c$$
(4.12)

The coefficients a_i, b_i , and c have been tabulated in reference [82]. In this research, the analytic expression was used to calculate the atomic scattering factors of Ni, Zr, and Hf.

When the x-ray energy is far from the absorption edges of the atoms in the sample, both f'(Q) and f''(Q) are small and almost Q-independent. Therefore, they have been evaluated and tabulated as constants for the $K\alpha$ energy (wavelength) of various commercial x-ray targets [83]. Table 4.1 gives the anomalous dispersion factors f' and f'' for Ni, Zr, and Hf at the wavelength of Ag-K α .



Figure 4.1: The density of amorphous Ni-Zr alloys. The polynomial fitting is shown as the solid line through the data points.

	Ni	Zr	Hf
Z	28	40	72
f'	0.261	-0.639	-0.890
_ <u>f"</u>	0.724	2.630	4.164

Table 4.1: The dispersion corrections at $\lambda = Ag \cdot K\alpha$

The incoherent scattering intensity that the detector "sees" can be expressed as

$$I_{inc}(Q) = \left(\frac{\lambda}{\lambda'}\right)^2 C(Q) \nu(\lambda') \tag{4.13}$$

where $(\lambda/\lambda')^2$ is the Breit-Dirac recoil factor [9], C(Q) is the Compton scattering intensity of the alloy, and $\nu(\lambda')$ is the band-pass function of the detector.

The Compton scattering intensities of the elements have been theoretically calculated by Cromer et al [82,84] and fitted to an analytic function [85]:

$$C_i(\frac{\sin\theta}{\lambda}) = Z - \sum_{j=1}^{5} a_j exp(-b_j \frac{\sin^2\theta}{\lambda^2})$$
(4.14)

where Z is the atomic number of the element, and the coefficients a_j and b_j have been tabulated in reference [85]. Using equation 4.14 the Compton scattering intensity of Ni, Zr, and Hf were calculated, and the Compton scattering intensity of the alloy is calculated by

$$C(Q) = \sum_{i} c_{i} C_{i} \left(\frac{\sin\theta}{\lambda}\right)$$
(4.15)

where c_i and C_i are, respectively, the atomic concentration and the Compton scattering intensity of the type-*i* atom.

The band-pass function $\nu(\lambda)$ represents the transmittance of the analysing crystal. As indicated previously, the analyzer used in this work is a graphite crystal, which is actually a mosaic of crystallites aligned with each other within a angle σ_{ω} . As a monochromator, such a pseudo single crystal has four to six times the reflectivity of a single crystal such as LiF, and gives a uniformly distributed diffraction beam. The resolution of the analyzer is characterized by the width of the band-pass function, which describes how well the hexagonal basal planes are aligned in the graphite crystal. The reflection plane of the monochromator is (220), corresponding to a d-spacing of 1.75Å. The rocking curve along [220] direction of the monochromator was measured using the high resolution double crystal diffractometer ¹. The result is shown in figure 4.2, where the solid line through the data points is the best fit to a Gaussian-function:

$$G(\omega) = Nexp(-\frac{\omega^2}{2\sigma_{\omega}^2})$$
(4.16)

where N is the scaling factor and σ_{ω} is the width of the Gaussian function. It was found that

$$\sigma_{\omega} = 0.218^{\circ} \tag{4.17}$$

The monochromator was used in the experiments to eliminate the radiation of unwanted wavelength, therefore, it is useful to convert equation 4.16 into a function of x-ray wavelength, λ . From the Bragg formula:

$$2dsin\theta_M = \lambda \tag{4.18}$$

it follows that

$$2d\cos\theta_M \Delta\theta_M = \Delta\lambda \tag{4.19}$$

where θ_M is the Bragg angle of the monochromator for planes with spacing d. From geometry

$$\omega = \Delta \theta_M \tag{4.20}$$

¹This experiment was kindly performed by T. Q. Gu on the double crystal diffractometer in the Physics Department, McGill University.



Figure 4.2: Band-pass function of the x-ray monochromator. The Gaussian fitting is shown as the solid line through the data points.

Using equation 4.16, 4.19, and 4.20, one obtains

$$G(\omega) = Nexp[-\frac{(\Delta\lambda)^2}{2(2d\cos\theta_M\sigma_\omega)^2}]$$
(4.21)

From 4.19 $\sigma_{\lambda} = 2d\cos\theta_M \sigma_{\omega}$ and equation 4.21 becomes

$$G(\omega) = Nexp(-\frac{(\Delta\lambda)^2}{2\sigma_{\lambda}^2})$$
(4.22)

Thus, the band-pass function of the monochromator, $\nu(\lambda)$, can be represented by the Gaussian function 4.22, i.e.

$$\nu(\lambda') = exp(-\frac{(\lambda - \lambda')^2}{2\sigma_{\lambda}^2})$$
(4.23)

where λ is the wavelength of the primary beam and $\lambda' = \lambda + 0.0486 sin^2 \theta$. Following equation 4.17, the band-pass width for the silver target is:

$$\sigma_{\lambda}^{Ag-K\alpha} = 0.0254 \mathring{A}$$

In this research, the highest scattering angle is $2\theta_{max} = 135^{\circ}$, which results in the largest wavelength shift, $\Delta \lambda_{max}$, for the Compton scattered radiation. Using 4.7 this gives $\Delta \lambda_{max} = 0.0486 sin^2 65^{\circ} = 0.03992 \text{\AA}$. Using Ag-K α radiation one has:

$$\nu(\lambda'_{max}) = exp(-\frac{0.04^2}{2 \times 0.0254^2}) = 0.289$$
(4.24)

This means that the monochromator cuts the Compton scattering intensity by at least 70% at $2\theta = 135^{\circ}$.² Figure 4.3 shows the Compton scattering intensity, C(Q), the total incoherent scattering intensity, $I_{inc}(Q) = C(Q)\nu(\lambda')$, compared with the intra-atomic scattering intensity, $< f^2 >$ for Ni_{0.33}Zr_{0.67}. Since the coherent

²Because of the defects in the analyser crystal, there are differences between the measured band-pass function and the Gaussian function at the tails. Therefore, the Gaussian fitting was only used to evaluate the band-pass width. The incoherent scattering intensity was calculated using the measured band-pass function.



Figure 4.3: The incoherent scattering of $Ni_{0.33}Zr_{0.67}$ compared with the intra-atomic scattering intensity, $\langle f^2 \rangle$. Solid line: $I_{inc}(Q)$, dashed line: C(Q) and dotted line: $\langle f^2(Q) \rangle$.

scattering oscillates about $\langle f^2(Q) \rangle$ and is essentially equal to $\langle f^2(Q) \rangle$ at high Q it can be seen that the diffracted beam monochromator significantly reduces the incoherent scattering correction for values of $Q > 8\dot{A}^{-1}$.

The "multiple scattering" contribution in equation 4.1 is due to x-rays which are scattered more than once while passing through the sample. Multiple scattering of x-rays is a complicated process, fortunately, the magnitude of the multiple scattering is small and it is sufficient to consider only double scattering [14]. The double scattering intensity can be calculated in terms of a double integral of the square of the first order intensity [86-88], which includes I_{coh} and I_{inc} . Since I_{coh} oscillates about $\langle f^2 \rangle$, it is a reasonable approximation for amorphous samples to replace I_{coh} with $\langle f^2 \rangle$ in the double integral [86]. A program has been written to calculate the x-ray double scattering intensity for both the reflection and transmission mode, and it has been tested with the data provided in reference [9] (page 148). Figure 4.4 shows the ratio of double to single scattering intensities, R_{12} , for several alloys used in this research. R_{12} is found to be always less than 4%

The x-ray diffraction experiments in this research were carried out in air. At low angles the scattering from air can be as much as 10% of the sample scattering. Therefore it is necessary to subtract the air scattering intensity from the $I_{obs}(2\theta)$. Since there exists an absorption difference with or without the sample in the beam, the air scattering contribution to equation 4.1 is given by [7]:

$$I_{air} = I_{air}^{obs}(2\theta) \left[\frac{1}{2} + \left(\frac{1}{2} - \frac{t\cos\theta}{R\beta}\right)e^{-\frac{2\mu t}{sin\theta}}\right]$$
(4.25)

where I_{air}^{obs} is the air scattering intensity measured in the absence of the sample, t is the thickness of the sample, μ is the linear absorption coefficient of the sample, R is the radius of the diffractometer, and β is the angle subtended at the sample by



Figure 4.4: The ratio of double to single scattering intensity for $Ni_{0.33}(Zr_yHf_{1-y})_{0.67}$.

the detector slit.

The quantity I_b , in equation 4.3 represents the background which is mainly due to secondary fluorescence radiation. I_b is uniformly distributed over the entire angular range (the angular dependence of the scattering volume's size has been included in the absorption correction term). As discussed in reference [7] (page 493), the fluorescence effect is most severe when the atomic number of the target material, Z_{target} , is 2 or 3 larger than that of the elements in the sample, $Z_{element}$. This is why the data measured with Mo target is not used for this research ($\Delta Z = Z_{Mo} - Z_{Zr} = 2$). In that case, the background is as high as 25% of the total intensity and results in a serious reduction in the counting statistics. The fluorescent scattering is generally small when $\Delta Z > 4$. Therefore, a silver target was used in this research ($\Delta Z \ge 7$). In this case, the background I_b is about 8% of the total scattered intensity. In the literature, the background is sometimes measured by an additional experiment. Here, I_b is treated as a fitting parameter.

Finally, the normalization factor, N, in equation 4.3 is proportional to the primary beam intensity, the total number of atoms in the sample and the thickness of the sample. Since the primary beam intensity is unknown, N remains as another fitting parameter.

From equation 4.1 and the above discussion it is apparent that $I_{coh}(Q)$ can be obtained from the observed intensity once the parameters N and I_b are determined. In the literature, several normalization methods have been used to derive the total structure factor from the experimental intensity [6,14,47]. In this research, both the high-angle fitting procedure and the Krogh-Moe-Norman (KMN) method have been used to normalize the x-ray diffraction data.

At large values of Q, which correspond to large values of 2θ , the structure factor has a limiting value of unity. Therefore, at high θ the right hand side of equation 4.1 becomes

$$NP\{A < f(Q)^{2} > +A'I_{inc}(Q) + I_{mul}(Q)\} + I_{air} + I_{b} = I_{fit}(2\theta)$$
(4.26)

By choosing different values of N and I_b a value of $I_{fit}(2\theta)$ may be calculated. $I_{fit}(2\theta)$ may then be compared with I_{obs} at high values of 2θ . The optimum values of N and I_b can be determined by minimizing the quantity χ^2 , where

$$\chi^{2} = \sum_{i} \frac{1}{\sigma_{i}^{2}} [I_{obs}(2\theta_{i}) - I_{fit}(2\theta_{i})]^{2}$$
(4.27)

In equation 4.27, *i* is the index of data points, σ^2 is the experimental error of I_{obs} at $2\theta_i$. This method of scaling the diffraction intensity is called "the high-angle fitting method", because the summation in equation 4.27 is usually carried out in an appropriate high-angle range where $I_{obs}(2\theta)$ does not strongly oscillate about $I_{fit}(2\theta)$. Since the fitting function $I_{fit}(2\theta)$ is actually the asymptote of $I_{obs}(2\theta)$, a minimized χ^2 does not necessarily lead to correct values of N and I_b . In a limited range of 2θ the solution to equation 4.26 may not be unique. Therefore, the range of 2θ over which the fitting procedure is performed plays an important role in determining N and I_b . As shown in figure 4.5, in the range of $80^\circ \leq 2\theta \leq 130^\circ$, $I_{fit}(2\theta)$ fits well to $I_{obs}(2\theta)$ and $\chi^2 = 1.09$. However, I_{fit} apparently underestimates I_{obs} in the range $2\theta < 60^\circ$. In this case, the derived S(Q) oscillates above unity and begins to modulate about unity only in the fitting range (see figure 4.6). In this research, the parameters N and I_b^2 are first determined by minimizing χ^2 in equation 4.27 over

²Considering there may exist some unknown scattering from the objects around the goniometer, I_b was expressed by a polynomial: $a_o + a_1 \times 2\theta + a_2 \times (2\theta)^2$. For all the samples, a_2 was found to be zero and a_1 is usually very small compared to a_o .



Figure 4.5: Results of fitting the observed intensity in a limited high angle region. Note that the peak area above the fitting curve is much greater than that below the fitting curve. A correct fit would have the two areas about equal.



Figure 4.6: The total structure factor resulting from a bad normalization.

the range $2\theta_3 \leq 2\theta \leq 130^\circ$, where $2\theta_3$ is at the beginning of the third maximum of $I_{obs}(2\theta)$ curve. The KMN method was then used to refine these fitting parameters.

The KMN normalization method was first suggested by J. Krogh-Moe [89]. The details of this method can be found in reference [89,90]. Its central formula can be obtained as follows.

From equation 2.19, one has

$$4\pi r^2 \rho_o[g(r) - 1] = \frac{2r}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) dQ$$
(4.28)

OL

$$2\pi^{2}\rho_{o}[g(r)-1] = \int_{0}^{\infty} Q^{2}[S(Q)-1] \frac{\sin(Qr)}{Qr} dQ \qquad (4.29)$$

The fact that atoms do not approach each other within the atomic core diameter suggests that

$$\lim_{r \to 0} g(r) = 0 \tag{4.30}$$

On the other hand, mathematically, one has

$$\lim_{r \to 0} \frac{\sin Qr}{Qr} = 1 \tag{4.31}$$

Using 4.30 and 4.31, in the low-r range, 4.29 is reduced to

$$-2\pi^{2}\rho_{o} = \int_{o}^{\infty} Q^{2}[S(Q) - 1]dQ$$
(4.32)

In Faber-Ziman formalism, one has

$$S(Q) - 1 = \frac{I_{coh} - \langle f^2(Q) \rangle}{\langle f(Q) \rangle^2}$$
(4.33)

Let $I_{cor} = (I_{obs} - I_{air} - I_b)/AP$, equation 4.1 becomes ⁴:

$$\alpha I_{cor} = I_{coh}(Q) + I_{mul}(Q) + I_{inc}(Q)$$
(4.34)

⁴The difference between the absorption correction for coherent and incoherent scattering is less than 1% and is neglected in equation 4.34.
where α is the reciprocal of the normalization factor N. From 4.33 and 4.34 it follows that

$$S(Q) - 1 = \frac{\alpha I_{cor} - \langle f^2(Q) \rangle - I_{mul}(Q) - I_{inc}(Q)}{\langle f(Q) \rangle^2}$$
(4.35)

Substituting 4.35 into 4.32 one has

$$2\pi^{2}\rho_{o} = \int_{o}^{\infty} Q^{2} \frac{\alpha I_{cor} - \langle f^{2}(Q) \rangle - I_{mul}(Q) - I_{inc}(Q)}{\langle f(Q) \rangle^{2}} dQ$$
(4.36)

Since the quantity $\langle f(Q) \rangle^2$ rapidly decreases with increasing Q, the errors in the observed intensity or I_{cor} can be greatly exaggerated by the factors Q^2 and $\frac{1}{\langle f(Q) \rangle^3}$ in 4.35. In order to reduce the enhancement, a damping factor $e^{-\gamma Q^2}$ is introduced and 4.36 is re-written as

$$2\pi^{2}\rho_{o} = \alpha \int_{Q_{\min}}^{Q_{\max}} Q^{2} \frac{I_{cor}}{\langle f(Q) \rangle^{2}} e^{-\gamma Q^{2}}$$
(4.37)

$$-\int_{Q_{\min}}^{Q_{\max}} Q^2 \frac{\langle f^2(Q) \rangle e^{-\gamma Q^2} - I_{mul}(Q) - I_{inc}(Q)}{\langle f(Q) \rangle^2} dQ \qquad (4.38)$$

The parameter γ is typically less than 0.01 and does not have to be accurately determined. In this work, the quantity I_b which is mainly due to the fluorescent scattering is unknown, therefore, it is rather difficult to evaluate the normalization parameter N by the KMN method ⁵. However, equation 4.38 provides a cross-check on the uniqueness of the parameters determined by the high-angle fitting method.

For all the samples, the quantity N and I_b in equation 4.3 were first determined using the high-angle fitting procedure. I_b was then used in equation 4.38 to calculate the parameter α . N and I_b were slightly adjusted (the adjustment usually causes little change of the χ^2) so that α becomes consistent with $\frac{1}{N}$ within $\pm 1\%$. The damping factor γ was typically ~ 0.01. As an example, the diffraction pattern



⁵In some previous work, I_b was obtained from additional measurements and then the KMN method was used to calculate the parameter α .

and the correct fitting function of Ni_{0.33}Zr_{0.67} is shown in figure 4.7. The resulting total structure factor is shown in figure 4.8. It should be noted that the fitting and refining procedure was carried out with the quantities in equation 4.3 and 4.27 being functions of 2 θ . The structure factor was determined first as a function of 2 θ . $S(2\theta)$ was then converted into S(Q) with equally spaced points in Q-space using a cubic spline interpolation method. $\Delta Q = 0.05 \text{\AA}^{-1}$ was chosen to correspond to the experimental resolution.

4.1.2 Reduction of neutron diffraction data

In conventional neutron diffraction experiments, the observed intensity can be expressed in terms of the Faber-Ziman total structure factor ⁶, S(Q), as [14]:

$$I_{obs}(2\theta) = NA[\langle b_c^2 \rangle + (S(Q) - 1) \langle b_c \rangle^2 + \langle b_i^2 \rangle + I_{mul}] + I_b$$
(4.39)

where:

Ν	=	The normalization factor;
Α	=	The absorption factor;
b_c^2	=	$\sum_{p} c_{p} (b_{c}^{p})^{2}$, b_{c}^{p} is the neutron coherent scattering length of element p ;
$< b_c >$	=	$\sum_{p} c_{p} b_{c}^{p};$
$< b_i^2 >$	=	$\sum_{p} c_{p} (b_{i}^{p})^{2}, b_{i}^{p}$ is the neutron incoherent scattering length of element p;
Inul	=	The multiple scattering intensity;
Іь	=	The background.

⁶In a neutron diffraction experiment, energy transfer occurs between the neutron and the system. Therefore, an integrated intensity is measured at a given angle 2 θ . The integration over the energy transfer is performed by the detector so that an effective differential scattering cross section rather than a true static cross section is measured [91]: $I_{obs} \propto (\frac{d\omega}{d\Omega})_{eff} \propto \int_{-E/h}^{\infty} \frac{Q'}{Q_*} S(Q,\omega) f(\omega) d\omega$ where E is the energy of the incident neutrons, Q' and Q_o are the incident and diffracted wave numbers, and $f(\omega)$ is the energy dependence of the detector. For neutrons of $\lambda \sim 1 \dot{A}$, the scattering is centered around the elastic value since the incident energy, $E \sim 85meV$, is considerably larger than the energy transfer, $h\omega < 10meV$. In this case, the inelasticity (or the Placzek correction) can be neglected, i.e. the 'static approximation' applies in which $S(Q, \omega)$ reduces to S(Q).



Figure 4.7: A typical fitting result for evaluating the total structure factor.



Figure 4.8: A typical result of accurately evaluated total structure factor.

The normalization factor, N, is a constant which is proportional to the primary beam intensity and the number of scatterers.

The neutron scattering lengths b_c and b_i have been measured and tabulated in reference [92]. Table 4.2 lists b_c and b_i and the absorption cross section, σ_a , for Ni, Zr, and Hf. It shows that Hf has a very large absorption cross section, therefore, experiments using the samples containing Hf, e.g. Ni_{0.33}Hf_{0.67}, need a much longer time than that for Ni_{0.33}Zr_{0.67} to achieve reasonable statistics ⁷.

Table 4.2: The neutron scattering length of Ni, Zr, and Hf.

	Ni	Zr	Hf
b_{c} (fm)	10.3	7.16	7.77
b_i (fm)	6.43	0.40	4.55
σ_a (barn)	4.49	0.185	104.10

The multiple scattering intensity, I_{mul} , is small in comparison with other quantities in equation 4.39 [93]. As discussed in the literature [14,25,94], the ratio of multiple to single scattering intensity is Q-independent, i.e. $I_{mul} \propto (I_{obs} - I_b)/NA$ (see 4.39). Therefore, the multiple scattering correction can be combined with the normalization factor, N.

The quantity I_b can be measured in the absence of the specimen under the same instrumental conditions. Figure 4.9 shows the measured I_b together with the diffraction pattern of Ni_{0.33}Zr_{0.67}.

According to the discussion above, equation 4.39 can be re-written as

$$I_{obs}(2\theta) = N'A[\langle b_c^2 \rangle + (S(Q) - 1) \langle b_c \rangle^2 + \langle b_i^2 \rangle] + I_b$$
(4.40)

⁷Since the neutron coherent scattering lengths of Zr and Hf are almost the same, neutron isomorphous substitution of Zr by Hf will not create significant changes in the weighting factors. Therefore, isomorphous substituion was not used in neutron diffraction experiments.

and

$$I_{obs}(2\theta) \xrightarrow{Q \to \infty} N' A[\langle b_c^2 \rangle + \langle b_i^2 \rangle] + I_b$$

$$(4.41)$$

Here the normalization parameter, N', is the only unknown. N is determined using the high angle fitting procedure described in the preceding section, and the total structure factor S(Q) is evaluated from equation 4.39. As a typical result, the S(Q)of Ni_{0.33}Zr_{0.67} is shown in figure 4.10.

4.1.3 The reliability of S(Q)

Due to instrumental limitations and the accuracy with which the x-ray atomic scattering factor, Compton scattering intensity, neutron scattering length are known, various errors may be introduced in the determination of total structure factors. As discussed in chapter 1, small errors in the total structure factors can be greatly enhanced in determining the partial structure factors. Therefore, it is necessary to analyze the residual uncertainties in the total structure factors and, if it is possible, to minimize the errors before carrying out the evaluation of the partial structure factors.

In some cases, the errors in S(Q) are best detected by distortions and the appearance of ghosts in the function:

$$G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] sinQ\tau dQ \qquad (4.42)$$

where G(r) is called the "reduced atomic pair distribution function" and is related to the atomic pair distribution function, g(r) by

$$G(r) = 4\pi r \rho_o[g(r) - 1]$$
(4.43)



Figure 4.9: The neutron diffraction pattern of Ni_{0.33}Zr_{0.67} and the background.



Figure 4.10: The neutron diffraction total structure factor of Ni_{0.33}Zr_{0.67}.

In the following paragraphes, the sources of error in the total structure factors are analyzed in terms of the function G(r), and the reliability of S(Q) determined from various experiments is discussed.

The increment ΔQ

In a diffraction experiment, the intensity is usually measured at scattering angles with equal increment, $\Delta 2\theta$. Since the fitting procedure is to fit the experimental raw data, therefore the total structure factor is determined originally as a function of scattering angle. Using the relation $Q = 4\pi \sin\theta/\lambda$, $S(2\theta)$ is equivalent to a S(Q)with unequal increments of Q.

The numerical evaluation of the Fourier integral which convert a structure factors into the corresponding distribution function is commonly performed by computing the equivalent summation

$$\sum_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1] sinQr \Delta Q \tag{4.44}$$

Practical considerations require that the increment ΔQ be a constant. For an accurate evaluation, there should be many increments ΔQ per half cycle in sinQr. Therefore, ΔQ must be small enough so that $r\Delta Q$ will also be small relative to the period of sinQr (i.e. $2\pi/r$). If there are n increments of rQ in the period then $nrQ = 2\pi$. If n is less than 10 then serious distortion appears in G(r) [7,95]. For amorphous alloys, it is usually desirable to obtain the atomic distribution information up to r = 10Å. In this case, $\Delta Q = \frac{2\pi}{nr} = \frac{2\pi}{100} = 0.063$ Å⁻¹ and a value of $\Delta Q = 0.05$ Å⁻¹ is generally acceptable because $n = 4\pi$, i.e. there would still be about 12 increments in ΔQ per cycle in sin(Qr) for $r \sim 10$ Å.

In this research, the instrumental resolution δQ in various experiments is about

 $0.1 - 0.05 \dot{A}^{-1}$ ⁸. The total structure factor $S(2\theta)$ was converted into S(Q) with $\Delta Q = 0.05 \dot{A}^{-1}$ using the cubic spline interpolation.

Non-observable region

A universally encountered source of uncertainty in S(Q) is the experimentally limited Q-range, that is, S(Q) is evaluated over the range of Q_{min} to Q_{max} , rather than 0 to ∞ .

The lower limit Q_{min} excludes the small angle scattering intensity information, which results in long-period oscillations in the Fourier transform [7]. Fortunately, most amorphous alloys are homogeneous systems and therefore, the small-angle scattering is rather weak. Further more, in the Fourier transform, the integrand is Q[S(Q) - 1]sinQr; and when Q is small, the integrand is also small. Under these circumstances the scattering in the range $0 < Q < Q_{min}$ can be neglected [7,16,96].

The truncating of S(Q) at $Q = Q_{max}$ can be much more serious than that at $Q = Q_{min}$. It is known that when the amplitudes of S(Q) are still of appreciable size at Q_{max} , each major peak in the function G(r) is bracketed by several pairs of diffraction ripples (ghosts). Fortunately, when Q_{max} is larger than $\sim 8.0 \text{Å}^{-1}$, which is true in this research, the truncating effect is not great. Furthermore, the ghosts can be suppressed by applying a damping factor, $e^{-\gamma Q^2}$, to S(Q) in the Fourier integral. As indicated by Klug et al [7], a damping factor simply compensates the exaggerating effect of the factor $\frac{1}{\langle f^2 \rangle}$ to the errors in S(Q) (see equation 2.33). Both the factors $e^{-\gamma Q^2}$ and $\frac{1}{\langle f^2 \rangle}$ exert their greatest influence at larger values of Q, which accounts for the effectiveness of a damping function in suppressing spurious ripples

⁸In the conventional x-ray diffraction experiments, the angular acceptance of the detector is about 0.3° (see section 3.2). Since $\Delta Q = 4\pi \cos\theta \Delta\theta/\lambda$, $\lambda = 0.56084\dot{A}$, $\Delta Q \sim 0.1$ at $2\theta = 2\theta_{min} = 4^{\circ}$, and $\Delta Q \sim 0.05$ at $2\theta = 2\theta_{max} = 130^{\circ}$. The angular acceptance of the detector slit in the neutron diffraction experiments is $\leq 0.3^{\circ}$.

arising from series termination. In this work, the value of γ is typically 0.01 - 0.005 for the Fourier integral represented by 4.44. Figure 4.11 shows an example of the influence of the factor $e^{-\gamma Q^2}$ on the Fourier integral.

The reliability criterion

Since atoms do not approach each other within the atomic core diameter r_c the value of g(r) must be zero for $r \leq r_c$. Hence one has the relation (see equation 4.43 and reference [6]):

$$G(r) = -4\pi r \rho_o \qquad r \le r_c \qquad (4.45)$$

i.e. In the low-r region, G(r) is a straight line with a slope equal to $-4\pi\rho_o$. As discussed previously, the experimental G(r) often has wiggles in this region, due to the truncating of S(Q) at $Q = Q_{max}$ and the residual uncertainties in the S(Q). However, one can draw a line through the curve from 0 to the first minimum of G(r)and the slope of this line gives an estimate of the average number density, ρ_o (see figure 4.12). The ρ_o estimated this way gives a reliability criterion for the accuracy of S(Q). As shown in figure 4.12, the ρ_0 values obtained using equation 4.45 agree with those measured by Altounian *et al* within 5%.

The method proposed by Rahman [97] has been used to obtain an idea of the residual uncertainty in S(Q) due to the errors in the normalization. Again, from the fact that the atomic distribution function g(r) is zero within the atomic core diameter r_c , for all values of r less than r_c , equation 2.19 in chapter 2 can be rewritten as ⁹:

$$-\rho_o = \left(\frac{1}{2\pi^2 r}\right) \int_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1] \sin(Qr) dQ \tag{4.46}$$

⁹4.46 itself has also been frequently used as a reliability criterion. However, the value of the right hand side of 4.46 depends on the integration limits and hence the left hand side of 4.46 is not uniquely defined (see reference [6]).



Figure 4.11: The effect of the damping factor to the Fourier integral. The circles represents the result with $\gamma = 0$. The solid line (which is identical to that shown in figure 4.12) is obtained with $\gamma = 0.0081$.



Figure 4.12: The reduced atomic pair distribution function of $Ni_{0.33}Zr_{0.67}$. The number density of the alloy is estimated by the slope of the straight line in the low-r range.

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Multiplying both sides of equation 4.46 by exp(-iur) (u is a dummy variable in the integration) and integrating over r in a sphere of radius L, we get the following useful relation:

$$4\pi\rho_o L^3 \frac{J_1(\nu L)}{\nu L} = \frac{L}{\pi\nu} \int_{Q_{\min}}^{Q_{\max}} Q[S(Q) - 1] [J_o\{(Q + \nu)L\} - J_o\{(Q - \nu)L\}] dQ \quad (4.47)$$

where J_i is the ith spherical Bessel function ¹⁰, ν is an arbitrary number with dimensions of \dot{A}^{-1} , and L is a value less than the atomic core diameter. It has been demonstrated [6,76,97] that 4.47 can be used as a reliability criterion for the experimental structure factor of a non-crystalline system. The application of equation 4.47 to the analysis of liquid metal and various metallic glasses can also be found in references [16,98,99].

Let ε_{theor} and ε_{exp} denote, respectively, the left and right hand side of equation 4.47, the values of ε_{theor} and ε_{exp} have been calculated with a variety of values of ν and L for the total structure factors obtained in this work. The results for amorphous Ni_{0.33}Zr_{0.67}, Ni_{0.33}(Zr_{0.6}Hf_{0.4})_{0.67}, and Ni_{0.33}Hf_{0.67} are listed in Table 4.3, where ϵ is the correction factor to S(Q) so that the value of ε_{exp} agrees with that of ε_{theor} , within 1%. It is found that the typical values of $|\epsilon - 1|$ range from 0.01 to 0.04. This means that the total uncertainty in the S(Q) is 1 to 4%.

In summary, the total structure factors were derived from the diffraction data using the high angle and the KMN methods. The uncertainty in these total struc-

$$J_0(x) = \frac{\sin x}{x}$$
$$J_1(x) = \frac{\sin x - x\cos x}{x^2}$$

¹⁰The spherical Bessel functions J_0 and J_1 are given by:

ture factors is examined using the method proposed by Rahman [97]. An accuracy of better than 4% is achieved for all the total structure factors obtained in this work.

У	L(A)	ν (\dot{A}^{-1})	Etheor	Eerp	e
1.0	1.00	1.00	0.201	0.201	0.999
	1.00	1.50	0.176	0.177	0.993
	1.00	2.00	0.145	0.146	0.971
	2.00	2.00	0.155	0.156	0.981
0.6	1.00	1.00	0.205	0.206	0.992
	1.00	1.50	0.179	0.180	0.983
	1.00	2.00	0.148	0.149	0.971
	2.00	2.00	0.158	0.159	0.965
0.0	1.00	1.00	0.193	0.192	1.010
	1.00	1.50	0.169	0.168	1.015
	1.00	2.00	0.139	0.138	1.024
	2.00	2.00	0.149	0.150	0.988

Table 4.3: Check on the normalization of S(Q) for $Ni_{.33}(Zr_yHf_{1-y})_{.67}$ using the relation proposed by A. Rahman [97].

4.2 Evaluation of the partial structure factors

As discussed in chapter 2, each total structure structure factor of a binary amorphous system consists of three partial structure factors:

$$S(Q) = w_{11}S_{11}(Q) + 2w_{12}S_{12}(Q) + w_{22}S_{22}(Q)$$
(4.48)

where w_{ij} (i,j = 1 and 2) are the weighting factors. In the Faber-Ziman formalism, one has

$$w_{ij} = \frac{c_i c_j f_i f_j}{\langle f \rangle^2}$$
(4.49)

where c_i and f_i are, respectively, the atomic concentration and scattering factor of i type atom. f_i can be calculated using equation 4.12 and $\langle f \rangle = c_i f_i + c_j f_j$ can be evaluated. For a pseudo-binary system with isomorphous substitution, e.g. $\operatorname{Ni}_{x}(\operatorname{Zr}_{y}\operatorname{Hf}_{1-y})_{1-x}$, the partial structure factors $S_{NiZr}(Q) = S_{NiHf}(Q)$ and $S_{ZrZr}(Q) = S_{HfHf}(Q)$, as far as the microstructure is concerned. Let *i* denote Ni and *j* denote the mixture $\operatorname{Zr}_{y}\operatorname{Hf}_{1-y}$, one has

$$f_j = y f_{Zr} + (1 - y) f_{Hf} \tag{4.50}$$

and thus equation 4.48 and 4.49 are equally valid for the pseudo-binary alloy.

In principle, the partial structure factors can be evaluated from three independent measurements by solving the linear equations:

$$S_m(Q) = \sum_{i=1}^2 \sum_{j=1}^2 w_{ij}^m S_{ij}(Q) \qquad (m = 1, 2, 3)$$
(4.51)

where *m* is the index of the measurements. However, as discussed in chapter 1, there is usually very little contrast between the measurements. As a consequence, equation 4.51 is often ill-conditioned. The results obtained by directly solving equation 4.51 are usually physically meaningless. The partial structure factors presented in the literature are often said to be a least-square estimate of equation 4.51. However, mathematically it has been proved that [100,101] for ill-conditioned linear equations the least-square solution is expected to be a very poor representation of the true quantities $S_{ij}(Q)$ in equation 4.51.

In fact, there always exist some uncertainties in the experimental data S(Q)($\leq 4\%$ in this work). Therefore, the partial structure factors should be evaluated from

$$S_m(Q) = \sum_{i=1}^2 \sum_{j=1}^2 w_{ij}^m S_{ij}(Q) + E_m(Q) \qquad (m = 1, 2, 3) \qquad (4.52)$$

where $E_m(Q)$ is the error in $S_m(Q)$. 4.52 is a typical problem for which a biased estimate of $S_{ij}(Q)$ can be obtained using a mathematical treatment called "ridge

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regression analysis". This method minimizes the errors propagated from the $S_m(Q)$ to the $S_{ij}(Q)$ and gives an estimate of the uncertainties in the solution. The details of the ridge analysis can be found in the Appendix A.

For $Ni_{0.33}Zr_{0.67}$, eight independent experimental total structure factors are available for evaluating the partial structure factors, seven from x-ray isomorphous substitution and one from neutron diffraction (see figure 4.14). The corresponding weighting factors for the various total structure factors are listed in table 4.4.

Iosmorphous substitution is an attractive method because the experiments can be carried out simply on a conventional x-ray diffractometer. The substitution of Zr by Hf in metallic glasses has been widely used in previous studies, however, the reliability of this method has not been carefully examined. In this work, the partial structure structure factors of Ni_{0.33}Zr_{0.67} are evaluated from the total structure factors of Ni_{0.33}(Zr_yHf_{1-y})_{0.67}, y = 1.0, 0.6 and 0.0 using ridge analysis ¹¹. The results are shown in figure 4.13. The overall uncertainty in these partial structure factors is ~ 4%. To examine the reliability of this evaluation, the results were then used to synthesize all the remaining experimental data. The results are shown in figure 4.14 The synthesized x-ray total structure factors agree very well with the experimental data; the discrepancies being within the error bars of the $S_{ij}(Q)$ curves.

It is interesting to find that the S(Q) synthesized with the partial structure factors obtained using x-ray isomorphous substitution is in good agreement with that measured using neutron diffraction (see figure 4.14) except in the low-Q range where the synthesis failed to reproduce an observed small "pre-peak" in the neutron scattering.

¹¹The mathematical details of the calculation can be found in the Appendix A.

y	w_{NiNi}	w_{NiZr}	WZrZr
1.00	.0696	.3882	.5422
0.80	.0556	.3602	.5882
0.60	.0455	.3353	.6192
0.50	.0414	.32:40	.6346
0.30	.0348	.3032	.6620
0.15	.0308	.2891	.6801
0.00	.0274	.2762	.6964
neutrons	0.1750	.4867	.3383

Table 4.4: X-ray weighting factors of amorphous $Ni_{0.33}(Zr_yHf_{1-y})_{0.67}$ alloys at $Q = 0.00 \text{ Å}^{-1}$. The last entry gives the neutron weighting factors for $Ni_{0.33}Zr_{0.67}$.

Table 4.5: Weighting factors for the partial structure factors of amorphous $Ni_{0.87}Zr_{0.33}$ at Q = 0.0 Å⁻¹.

	w _{NiNi}	w _{NiZr}	wZrZr
^a Ni _{0.67} Zr _{0.33}	.3386	.4864	.1750
°Ni _{0.67} Hf _{0.33}	.1959	.4932	.3109
^b Ni _{0.67} Zr _{0.33}	.5507	.3828	.0665

a) X-ray diffraction measurements;

b) neutron diffraction measurements.



Figure 4.13: The partial structure factors of $Ni_{0.33}Zr_{0.67}$. The length of the vertical bars indicates the error in the partial structure factors.



Figure 4.14: The total structure factors for Ni_{0.33}Zr_{0.67}.

For various metallic glasses, a peak in the low-Q range $Q < 2\dot{A}^{-1}$) has been frequently observed in the total structure factors obtained by neutron diffraction but is absent in those obtained by x-ray diffraction. Such a pre-peak is usually attributed to the chemical short-range order in the metallic glass [33,38,102-104], however, as will be discussed in chapter 5, this attribution is found to be inconsistent with the results of this work.

It has been suggested that there maybe small differences (of the order of 10%) between the experimental data of x-ray diffraction and that of neutron diffraction [6]. This is presumbaly due to the different scattering mechanisms. X-rays are scattered by electrons and the diffraction intensity depends upon both the ion-ion and electron-electron correlations; whereas neutron diffraction reflects only the ionion correlation. However, the ion-ion, ion-electron, and electron-electron correlations in a non-crystalline material are not well understood and may or may not account for the pre-peak.

To further examine the reliability of the results shown in figure 4.13, the partial structure factors of Ni_{0.33}Zr_{0.67} were once again evaluated from the x-ray total structure factors of Ni_{0.33}Zr_{0.67} and Ni_{0.33}Hf_{0.67}, and the neutron total structure factor of Ni_{0.33}Zr_{0.67}. The results are shown in figure 4.15 (the circles) in comparison with the partial structure factors obtained using the isomorphous substitution method (solid lines). As expected, the two sets of partial structure factors are in good agreements except in the low Q range, where S_{NiNi} and S_{NiZr} obtained with the neutron measurements have a small pre-peak.

From the previous discussion, it is evident that:

• Isomorphous substitution of Zr by Hf is a reliable method for evaluating the partial structure factors of Ni-Zr glasses, provided that the smaller size of Hf



Figure 4.15: A comparison of the partial structure factors of $Ni_{0.33}Zr_{0.67}$ obtained using x-ray isomorphous substitution (solid lines) and the combination of x-ray and neutron diffraction (circles).

is considered (see below);

• Accurate partial structure factors can be obtained from combining the x-ray and neutron diffraction measurements.

Encouraged by the successful evaluation of the partial structure factors of Ni_{0.33}Zr_{0.67}, the partial structure factors of Ni_{0.67}Zr_{0.33} were obtained from the x-ray total structure factors of Ni_{0.67}Zr_{0.33} and Ni_{0.67}Hf_{0.33}, and neutron total structure factors of Ni_{0.67}Zr_{0.33}. The weighting factors are listed in table 4.5 and the results are shown in figure 4.16. The total uncertainty in these partial structure factors is ~ 3%.

The previous procedure, i.e. obtaining one set of $S_{ij}(Q)$ from more than one isomorphous substitution measurements and another set independently from combined x-ray and neutron diffraction measurements, was not used for Ni_{0.67}Zr_{0.33}. This is because the change of the weighting factors due to the isomorphous substitution is too small for the Ni-rich alloy. On the other hand, the neutron scattering length of Ni is 30% larger than that of Zr. Therefore, in the neutron diffraction measurement for Ni_{0.67}Zr_{0.33}, not only the weighting factors were changed significantly, but also a much better experimental statistics was achieved. Hence, a reliable evaluation of the partial structure factors for Ni_{0.67}Zr_{0.33} was obtained from combining the x-ray and neutron diffraction measurements.

It should be indicated that the atomic radius of hafnium is slightly smaller than that of zirconium, therefore, the total structure factors of $Ni_{0.33}(Zr_yHf_{1-y})_{0.67}$ and $Ni_{0.67}(Zr_yHf_{1-y})_{0.33}, y \neq 0$, should be corrected for the atomic size difference. This atomic size correction is found to be crucial in the evaluation of the partial structure factors using the isomorphous substitution of Zr with Hf.



Figure 4.16: The partial structure factors of $Ni_{0.67}Zr_{0.33}$. The length of the vertical bars indicates the error in the partial structure factors.

The atomic size difference β can be expressed by

$$\beta = \frac{r_{Z_r} - r_{Hf}}{r_{Z_r}} \tag{4.53}$$

For amorphous $Ni_x(Zr_yHf_{1-y})_{1-x}$ alloys, the correction in Q-space is

$$\frac{\Delta Q}{Q} = \beta(1-y) \tag{4.54}$$

It follows from equation 4.54 that $\Delta Q > 0$ if $y \neq 1$. It is true that the peaks of the total structure factors of Ni_x(Zr_yHf_{1-y})_{1-x}, x = 0.33 and 0.67, $y \neq 0$, shift slightly towards higher Q (see table 4.6). The importance of the atomic size correction can be readily realized from figure 4.17, which shows the partial structure factors of Ni_{0.33}Zr_{0.67} obtained using the total structure factors of Ni_{0.33}(Zr_yHf_{1-y})_{0.67}, y = 1.0, 0.6 and 0.0, assuming $\beta = 0.0$. One can see the serious splitting in the first peaks of the partial structure factors. Obviously, such a splitting in a partial structure factor is physically untrue.

у	$\overline{Q_1}(A^{-1})$	$Q_2(A^{-1})$	$Q_3(A^{-1})$	Q_4 (A^{-1})
1.00	2.55	4.35	6.15	8.05
0.80	2.55	4.35	6.15	8.10
0.60	2.60	4.40	6.20	8.15
0.30	2.60	4.40	6.20	8.15
0.15	2.60	4.40	6.25	8.20
0.00	2.60	4.40	6.25	8.20

Table 4.6: Peak positions in the total structure factors of $Ni_{0.33}(Zr_yHf_{1-y})_{0.67}$.

Since neither r_{Zr} nor r_{Hf} are known accurately, the parameter β is adjusted according to the following physical constraints:

1. The peak positions of Ni_{0.33}(Zr_yHf_{1-y})_{0.67}, $y \neq 0.0$, are made consistent with those of Ni_{0.33} $Zr_{0.67}$;



Figure 4.17: The partial structure factors of $Ni_{0.33}Zr_{0.67}$ evaluated assuming $\beta = 0.0$.

- 2. The total structure factors for y = 1.0 to 0.0 give the same number density estimate according to equation 4.46;
- 3. No splitting appears in the partial structure factors;

This procedure results in a well determined atomic size correction, $\beta = 0.0175$, to Hf in the pseudo-binary glasses Ni_{0.33}(Zr_yHf_{1-y})_{0.67} and Ni_{0.67}(Zr_yHf_{1-y})_{0.33}, i.e. in these metallic glasses, the Hf atom is 1.75% small that the Zr atom. The partial structure factors shown in figure 4.13 and 4.16 are obtained with $\beta = 0.0175$.

4.3 Summary

As indicated in chapter 1, a reliable evaluation of the partial structure factors lies in two factors: the reliability of the original total structure factors and the contrast among the total structure factor measurements. In section 4.1 and 4.2 we have demonstrated how to normalize the diffraction data accurately to obtained the total structure factors. We further carefully examined the reliability of the derived total structure factors in section 4.1. An accuracy of better than 4% is found for all the total structure factors. In section 4.2, the contrast among these total structure factors is presented by the difference between their weighting factors. The contrast between the x-ray and neutron diffraction data is as high as 80%. The partial structure factors of Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} are successfully evaluated using combined x-ray and neutron diffraction. The total uncertainty is ~ 4%. The difference between the weighting factors of the isomorphous substitution total structure factors, additional experimental data were used and hence the three partial structure factors of Ni_{0.33}Zr_{0.67} were also evaluated independently from seven isomorphous substitution measurements. The results are consistent with the evaluation using combined x-ray and neutron diffraction. It is evident that accurate partial structure factors can be obtained using isomorphous substitution provided that the slight size difference between the isomorphous substituents is considered.

Chapter 5

Results and discussion

It was pointed out in chapter 2 that the atomic structure of a metallic glass can be described by the following quantities:

- The Faber-Ziman total structure factor, S(Q), and the total radial distribution function, RDF(r);
- The Faber-Ziman partial structure factors, $S_{ij}(Q)$, and the partial radial distribution functions, $RDF_{ij}(r)$.
- The Bhatia-Thornton partial structure factors, $S_{n,c}(q)^{-1}$.

The S(Q) and RDF(r) for melt-spun Ni_xZr_{1-x} (x = 0.25, 0.33, 0.37, 0.45, 0.50, 0.67) and sputtered Ni_xZr_{1-x} (x = 0.31, 0.36, 0.46, 0.53, 0.66, 0.75, 0.86) are obtained from various diffraction experiments. The results are presented in section 5.1. Based on the compositional dependence of the S(Q) and RDF(r); a comparison between the atomic structure of melt-spun and sputtered Ni-Zr glasses is made in section 5.2. The $S_{ij}(Q)$ and $RDF_{ij}(r)$ for Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} obtained in this work are presented in section 5.3. These results allow, for the first time, a discussion

¹Though the Faber-Ziman and Bhatia-Thornton partial structure factors can be mutually transformed by linear relations, the $S_{n,c}(Q)$ are found superior to the $S_{ij}(Q)$ when dealing with the chemical short-range order in amorphous materials.

of the composition dependence of the Faber-Ziman partial structure factors. In section 5.3.2, the $RDF_{ij}(r)$ of Ni-Zr glasses are compared with the local atomic structure of the corresponding crystalline solids. The chemical short-range order in Ni-Zr metallic glasses is discussed in section 5.4.1 using the $S_{n,c}(Q)$ which have been calculated from the $S_{ij}(Q)$. Finally, the relationship between the "pre-peak" and the chemical short-range order is discussed in section 5.4.2.

It should be pointed out in advanced that no differences are observed between the atomic structure of the melt-spun and sputtered Ni-Zr glasses as will be shown in section 5.2. Therefore, in the discussions of this chapter, the melt-spun and sputtered samples are not distinguished.

5.1 S(Q) and RDF(r)

5.1.1 The total structure factor S(Q)

The Faber-Ziman total structure factors of amorphous alloys $\operatorname{Ni}_{x}\operatorname{Zr}_{1-x}$, $0.25 \leq x \leq 0.86$, were obtained from x-ray diffraction measurements in the range $0.08 \leq Q \leq 20\dot{A}^{-1}$. Figure 5.1 shows the total structure factor S(Q) for each of the compositions in the range $0 \leq Q \leq 10\dot{A}^{-1}$, since for all the compositions the S(Q) oscillates about unity and becomes flat when $Q \geq 10\dot{A}^{-1}$.

As can be seen from figure 5.1, the total structure factor features a relatively strong first peak and a shoulder on the high-Q side of the second peak. A shoulder on the second peak of the S(Q) is common in metallic glasses whereas it is usually absent in liquid metals. It is interesting to note that for x = 0.86, i.e. the sample contains almost one type of atoms, Ni, the shoulder remains pronounced. The third peak is weak and after the third peak the amplitude becomes very small. It also



Figure 5.1: The Faber-Ziman total structure factors of melt-spun $Ni_{x_m}Zr_{1-x_m}$. (dashed lines) and sputtered $Ni_{x_m}Zr_{1-x_m}$ (solid lines). The results are offset by 1 for each composition.

should be mentioned that the value of the total structure factor before the first peak is almost constant and very small $(S(Q) \sim 0.2)$.

Besides the common features described above, the S(Q) of Ni-Zr glasses exhibit a clear compositional dependence. As one can see from figure 5.1, the oscillation period of the S(Q) increases with increasing Ni concentration. As a result, the peaks of the S(Q) shift towards higher-Q due to the closer packing of the smaller Ni atoms. The height of the peaks also changes with composition but in a nonlinear fashion. As shown in figure 5.1, the amplitude of oscillations becomes the lowest at x = 0.45. Further evidence of the compositional dependence of S(Q) is that the shape of the second peak changes dramatically with Ni concentration. For the Zr-rich samples, the second peak looks almost like a single peak but with a small shoulder while for the Ni-rich samples the second peak has a very pronounced shoulder. Around the equiatomic composition, the second peak is broad and essentially flat. For x = 0.86, the position ratio of the two subpeaks is equal to $0.86 \simeq \sqrt{3}/2$. This means that the shoulder is due to the two possible nearest neighbor configurations of equal sized balls (see the diagram on page 93). Since Zr atoms are 30% larger than Ni atoms and the second peak of the S(Q) for Ni_{0.86}Zr_{0.14} is located at a much higher Q position than that of the other compositions, the shoulder is clearly attributed to the configuration of Ni atoms. This characteristic is not suprising due to the predominace of Ni atoms in the Ni_{0.86}Zr_{0.14} glass. For x = 0.25, the shoulder appearing in the second peak is clear enough to allow an estimate to be made of the position ratio of the two subpeaks giving a value of $\sim 0.88 \simeq \sqrt{3}/2$. In analogy to the situation for Ni_{0.86}Zr_{0.14}, this shoulder is due to the configuration of Zr atoms in Ni_{0.25}Zr_{0.75} glass. Thus, the dramatic change in the shape of the second peak of S(Q) corresponds to a smearing caused by the different sized atoms in both configurations.

5.1.2 The total radial distribution functions RDF(r)

The Fourier transform of the S(Q) gives the total radial distribution function $RDF(r) = 4\pi r^2 \rho(r)$, where $\rho(r)$ is the total atomic correlation function (see chapter 2). The nearest neighbor coordination number n_1 can be obtained from integrating the first peak of the RDF(r). The quantities RDF(r) and n_1 provide a general insight into the local topological order in amorphous materials.

Figure 5.2 shows the total radial distribution functions corresponding to each of the S(Q) shown in figure 5.1. Three broad peaks are observed in the range $r \leq 8\dot{A}$. In general, only the first peak is useful for the analysis of the local atomic configuration. It can be seen from figure 5.2 that for all the compositions except x = 0.86, the first peak of the RDF(r) consists of two subpeaks, one at $r \sim 2.75 \text{\AA}$ and the other at $r \sim 3.2 \text{\AA}$. The atomic diameters of Ni and Zr atoms are about 2.5Å and 3.2Å, respectively. Therefore, the subpeak at 2.75Å is due to the first atomic shell centered at Ni atoms and that at 3.2Å is attributed to the atomic shell centered at Zr atoms. As a consequence, the height of the first subpeak increases with increasing Ni concentration whereas the opposite holds for the second subpeak. It is of interest to point out that these two subpeaks have the same height at x = 0.45rather than at x = 0.50. For x = 0.86, the first peak of the RDF(r) is essentially a symmetric single peak. The peak position which is at 2.6Å is much lower than the first subpeak of the RDF(r) for $x \leq 0.86$. This is clearly due to the dominant contributions to the RDF(r) from the Ni atoms. It indicates that in the alloys with $x \ge 0.86$, the small number of Zr atoms have little effect on the RDF(r).



Figure 5.2: The radial distribution functions of melt-spun $Ni_{x_m}Zr_{1-x_m}$ (dashed lines) and sputtered $Ni_{x_m}Zr_{1-x_m}$ (solid lines). The results are offset by 20 for each composition.

Figure 5.4 shows the total nearest neighbor coordination number N_1 obtained for each of the RDF(r) as a function of Ni concentration. Initially, N_1 increases rapidly with Ni concentration. N_1 reaches a maximum value at x = 0.45. With further increasing Ni concentration N_1 gradually decreases. It is clear that N_1 has a strong compositional dependence. The average value of N_1 is about 14.

The above discussions on the compositional dependence of the S(Q), RDF(r), and n_1 reveals that there is a structural turning point in Ni-Zr glasses for the alloy with 45% Ni. This characteristic should have an influence on various properties of the material. Indeed, the electrical resistivity and thermoelectric power of Ni-Zr glasses at room temperature measured by Altounian *et al* [62] show the same feature as shown in figures 5.5 and 5.6. Such striking similarity among the compositional dependence of these three quantities suggests a close relationship between the near neighbor atomic structure and the electrical properties of Ni-Zr metallic glasses.

5.2 A comparison of the atomic structures of melt-spun and sputtered Ni-Zr glasses

Melt-spinning and magnetron sputtering are two very different techniques of producing metallic glasses. With the melt-spinning method the metallic glass is made from a molten alloy; while with the sputtering technique an amorphous film is formed from the gas phase. It is, therefore, interesting to examine whether the preparation method influences the atomic structure of the as-made Ni-Zr metallic glasses.

Form figure 5.1 and 5.2 one can see that the S(Q) and RDF(r) of melt-spun and sputtered samples with similar composition look almost identical. The main



Figure 5.3: The two possible nearest neighbor configurations of equal sized balls (a = radius).



Figure 5.4: The total coordination number of nearest neighbor in Ni-Zr glasses.



Figure 5.5: Electric resistivity of Ni-Zr metallic glasses at room temperature as a function of composition. (After Altounian et al [62])



Figure 5.6: Thermoelectric power of Ni-Zr metallic glasses at room temperature as a function of composition. (After Altounian et al [62])

peak of the S(Q) for melt-spun sample is a few percent lower than that for the corresponding sputtered sample. This is probably due to resolution effects. As indicated in chapter 3, the ribbon: were arranged to overlap with each other to make an x-ray diffraction sample. The overall uniformity of such a sample was found to be satisfactory. However, due to the overlaps, the thickness variation along the direction perpendicular to the beam slightly worsens the focus geometry and results in reduced resolution of the diffraction intensity in comparison with the much more uniform sputtered samples. As shown in figure 5.2, the RDF(r) is relatively insensitive to this resolution effect.

More detailed structural information can be found from the nearest neighbor coordination number n_1 . As discussed in the previous section, n_1 is a function of alloy composition. In figure 5.4, which shows n_1 versus composition x, the solid squares are from the melt-spun samples and the circles are from sputtered films. The excellent match between the squares and circles indicate that the melt-spun and sputtered amorphous Ni-Zr alloys prepared in this work have the same nearest neighbor coordination number.

The crystallization enthalpy can also be used as a measure of the similarity in the structure of amorphous materials (see chapter 3). The crystallization enthalpy, ΔH , of the melt-spun and sputtered Ni-Zr metallic glasses has been measured using differential scanning calorimetry (DSC). The results are shown in figure 5.7. Altounian *et al.* [66] have systematically studied the crystallization behavior of melt-spun Ni-Zr metallic glasses. Their results are shown in figure 5.7 along with the error bars given in their measurements. As can be seen, our results are consistent with those of Altounian [66] for melt-spun ribbons and sputtered films.

The above discussion leads to the conclusion that there is no difference between



Figure 5.7: Enthalpy associated with crystallization for Ni-Zr glasses. Solid circles: melt-spun ribbons; open circles: sputtered filmes; triangles: taken from reference [66].
the atomic structure of melt-spun and sputtered Ni-Zr glasses.

5.3 $S_{ij}(Q)$ and $RDF_{ij}(r)$

5.3.1 The Faber-Ziman partial structure factors $S_{ij}(Q)$

To gain a complete insight into the atomic structure of an amorphous alloy the partial structure factors must be obtained. The procedure for evaluating the Faber-Ziman partial structure factors for Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} has been described in detail in section 4.2. The reliability of these partial structure factors was carefully examined. Figure 5.8 displays these two sets of Faber-Ziman partial structure factors together, where the solid lines are for Ni_{0.33}Zr_{0.67} and the dashed lines for Ni_{0.67}Zr_{0.33}. The position and height of the first peak for each of the $S_{ij}(Q)$ are listed in table 5.2.

Table 5.2: Peak positions of the partial structure factors of $Ni_{z}Zr_{1-z}$.

	S _{NiNi}		S _{NiZr}		SZTZT	
x	0.33	0.67	0.33	0.67	0.33	0.67
Q_1	2.65	2.95	2.65	2.90	2.55	2.75
$S_{ij}(Q_1)$	2.24	3.38	2.34	2.59	2.88	2.57

 Q_1 = the position of the first peak in A^{-1} ; $S_{ij}(Q)$ = the height at $Q = Q_1$.

From figure 5.8 and table 5.2, it is seen that the partial structure factors of Ni-Zr glasses have strong compositional dependence. As the composition changes from Ni_{0.33}Zr_{0.67} to Ni_{0.67}Zr_{0.33}, the position of the first peak shifts to higher Q by 11%, 10% and 9% for the Ni-Ni, Ni-Zr and Zr-Zr partial structure factors, respectively. For the two alloys, the height of the first peak in Ni-Zr and Zr-Zr partial structure



Figure 5.8: The partial structure factors of $Ni_x Zr_{1-x}$. solid lines: x = 0.33; dashed lines: x = 0.67.

factors is relatively the same. However, the height of the first peak in the Ni-Ni partial structure factor shows a more than 30% increase as x changes from 0.33 to 0.67. The variations of $S_{NiNi}(Q)$, $S_{NiZr}(Q)$ and $S_{ZrZr}(Q)$ with composition are further discussed below.

i. $S_{NiNi}(Q)$: As shown in figure 5.8a, the $S_{NiNi}(Q)$ of Ni_{0.33}Zr_{0.67} has an asymmetric first peak at 2.65Å⁻¹. The second peak is broad and flat. The amplitude of oscillations becomes almost zero for $Q \ge 8Å^{-1}$. The $S_{NiNi}(Q)$ of Ni_{0.67}Zr_{0.33} looks very different from that of Ni_{0.33}Zr_{0.67}. It has a relatively strong symmetric first peak at 2.95Å⁻¹. The second peak has a very pronounced shoulder on the high-Q side. It is not surprising that such a shoulder appears in the partial structure factor S_{NiNi} of Ni_{0.67}Zr_{0.33} glass. As mentioned in section 5.1.1, the total structure factor for Ni_{0.86}Zr_{0.14} is dominanted by the contributions from the Ni atoms. Therefore, this alloy can be approximately considered as a one-component system, i.e. Ni glass. There is a strong shoulder in the second peak of the total structure factor for Ni_{0.86}Zr_{0.14}. The comparison of the $S_{NiNi}(Q)$ for Ni_{0.67}Zr_{0.33} and the S(Q) of Ni_{0.86}Zr_{0.14} is shown in figure 5.9. The similarity between the second peaks of the two structure factors confirms that the shoulder feature is due to the Ni-Ni correlation in the glass. This Ni-Ni correlation becomes weak as the Zr content increases.

ii. $S_{ZrZr}(Q)$: The partial structure factors $S_{ZrZr}(Q)$ for Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} are shown in figure 5.8c. For both the compositions, $S_{ZrZr}(Q)$ has a relatively strong and symmetric first peak and oscillates up to $10\AA^{-1}$. However, there are significant differences between the $S_{ZrZr}(Q)$ for x = 0.33 and 0.67. The oscillation period of the $S_{ZrZr}(Q)$ for Ni_{0.33}Zr_{0.67} is much greater than that for Ni_{0.67}Zr_{0.33}. The second



Figure 5.9: The Faber-Ziman partial structure factors $S_{NiNi}(Q)$ of $Ni_{0.67}Zr_{0.33}$ comparing to the total structure factor S(Q) of $Ni_{0.86}Zr_{0.14}$. Q_1 is the position of the first peak.



Figure 5.10: The Faber-Ziman partial structure factors $S_{NiNi}(Q)$ of $Ni_{0.33}Zr_{0.67}$ comparing to the total structure factor S(Q) of $Ni_{0.25}Zr_{0.75}$. Q_1 is the position of the first peak.

peak of the $S_{Z_rZ_r}(Q)$ for x = 0.33 has a weak shoulder while that for x = 0.67 looks essentially symmetric. It is interesting to compare the $S_{Z_rZ_r}(Q)$ for x = 0.33 to the total structure factor S(Q) of Ni_{0.25}Zr_{0.75} (see figure 5.10). Similar to the situation for $S_{NiNi}(Q)$ of the Ni-rich sample, the $S_{Z_rZ_r}(Q)$ of Ni_{0.33}Zr_{0.67} looks much the same as the S(Q) of the Zr-rich sample, Ni_{0.25}Zr_{0.75}. Hence, the shoulder which appeares in the second peak of the $S_{Z_rZ_r}(Q)$ and the S(Q) of Zr-rich samples is due to the correlation among the Zr atoms.

iii. $S_{NiZr}(Q)$: In comparison to the other two partial structure factors, the $S_{NiZr}(Q)$ is relatively less sensitive to composition. As shown in figure 5.8b, the $S_{NiZr}(Q)$ features three maxima in the range $Q \leq 8\dot{A}^{-1}$. Beyond this range, the oscillation of the $S_{NiZr}(Q)$ becomes almost zero. The $S_{NiZr}(Q)$ of Ni_{0.67}Zr_{0.33} looks sharper than that of Ni_{0.33}Zr_{0.67}, and the position of the first peak shifts by about 10% from x =0.33 to 0.67.

It is of interest to compare the partial structure factor $S_{NiZr}(Q)$ to the total structure factor S(Q) of Ni_{0.5}Zr_{0.5}. Figure 5.11 shows the $S_{NiZr}(Q)$ of Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} together with the S(Q) of Ni_{0.5}Zr_{0.5}. The three curves look very similar to each other. Since the compositions for the two partial structure factors are symmetrically distributed from x = 0.5, it is interesting to take the average of the $S_{NiZr}(Q)$ for x = 0.33 and x = 0.67 and compare it with the S(Q) of Ni_{0.5}Zr_{0.5}. The results is shown in figure 5.12. One can see the dramatic similarity between the two curves. This characteristic is probably due to the fact that the $S_{NiZr}(Q)$ is relatively insensitive to composition; on the other hand, as will be shown later, a nearly random mixture of the constituent atoms is retained in Ni-Zr glasses, therefore, in amorphous Ni_{0.5}Zr_{0.5}, the S(Q) is dominated by the partial structure factor $S_{NiZr}(Q)$. The average of the $S_{NiNi}(Q)$ and $S_{ZrZr}(Q)$ are shown in figure 5.13. As can be seen the two curves have inverted maxima and minima. Therefore, a synthesis using the average of the three partial structure factors of Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} would give results similar to the average of the S_{NiZr} only (see figure 5.14). The discrepancy in the amplitude of the first peak in the measured and synthesized S(Q) in figure 5.12 and 5.14 will be discussed later.

The composition dependence of $S_{ij}(Q)$ can also be seen by using the partial structure factors of Ni_{0.33}Zr_{0.67} to synthesize the total structure factor across the entire range of composition. The equivalent synthesis can be done using the partial structure factors for Ni_{0.67}Zr_{0.33}. The results of the synthesis are shown in figure 5.15. As can be seen from the figure each set of partial structure factors yields an excellent total structure factor for compositions near the composition of the partial structure factors. The agreement becomes progressively worse with increasing compositional difference. As shown in figure 5.4 there is a structural turning point at $x \sim 0.45$. In figure 5.15, for the alloys contains about 45% Ni, the main peaks in the two synthesized S(Q) appear on the each side of that in the measured S(Q), whereas for the Ni-rich or Zr-rich alloys, the main peaks in both the synthesized S(Q) are found to be at lower or higher Q than that in the measured S(Q). These results further show the strong compositional dependence of the Faber-Ziman partial structure factors of Ni-Zr glasses. To see whether this compositional dependence of $S_{ij}(Q)$ is linear, the linear combination of the two sets of $S_{ij}(Q)$ is used to synthesize the S(Q) for x = 0.5. The result is shown in figure 5.14. The large discrepancy in the amplitude of the first peak between the measured and synthesized S(Q) suggests that there is a non-linear feature in the composition dependence of the Faber-Ziamn



Figure 5.11: The $S_{NiZr}(Q)$ of $Ni_{0.33}Zr_{0.67}$ and $Ni_{0.67}Zr_{0.33}$ comparing to the S(Q) of $Ni_{0.5}Zr_{0.5}$.



Figure 5.12: The measured Faber-Ziman total structure factors of $Ni_{0.5}Zr_{0.5}$ comparing to the average of the $S_{NiZr}(Q)$ for $Ni_{0.33}Zr_{0.67}$ and $Ni_{0.67}Zr_{0.33}$ (i.e. 50% S_{NiZr} for $x=0.33 + 50\% S_{Nizr}$ for x=0.67).



Figure 5.13: The S(Q) of $Ni_{0.5}Zr_{0.5}$ comparing to the average of the $S_{ii}(Q)$ (i = Ni and Zr) for $Ni_{0.33}Zr_{0.67}$ and $Ni_{0.67}Zr_{0.33}$ (i.e. 50% S_{ii} for x=0.33 + 50% S_{ii} for x=0.67).



Figure 5.14: The S(Q) of $Ni_{0.5}Zr_{0.5}$ comparing to the linear synthesis using the partial structure factors of $Ni_{0.33}Zr_{0.67}$ and $Ni_{0.67}Zr_{0.33}$.



Figure 5.15: The measured and synthesized Faber-Ziman total structure factors of amorphous Ni_xZr_{1-x} . solid line = measured data; dashed line = calculation using the $S_{ij}(Q)$ of $Ni_{0.33}Zr_{0.67}$; dotted line = calculation using the $S_{ij}(Q)$ of $Ni_{0.67}Zr_{0.33}$.

partial structure factors of Ni-Zr glasses.

As indicated in chapter 2, the Faber-Ziman structure factors do not explicitly involve the atomic composition. This is probably the reason that many previous structural studies of metallic glasses used the concentration technique to derive the Faber-Ziman partial structure factors. In this technique the weighting factors are varied by changing the alloy composition c assuming that the partial structure factors are independent composition. However, from the discussion above, it is clear that the partial structure factors of Ni-Zr metallic glasses have strong compositional dependence. Therefore, it is inappropriate to use the concentration technique to evaluated the partial structure factors in Ni-Zr glasses. In fact, it is probably dangerous to use the concentration technique for any other system.

5.3.2 The partial radial distribution functions $RDF_{ij}(r)$

The partial radial distribution function $RDF_{ij}(r)$ corresponds to the number of jtype atoms in the spherical shell between r and r + dr centered at an i-type atom. The $RDF_{ij}(r)$ is obtained from the Fourier transform of the $S_{ij}(Q)$. The partial coordination number n_{ij} in the nearest neighborhood can be obtained by integrating the first peak of the $RDF_{ij}(r)$. In this section, the atomic structure of amorphous Ni-Zr glasses is discussed in terms of the partial radial distribution functions. The results are also compared to the previous studies on the amorphous Ni_{0.33}Zr_{0.67} and crystalline NiZr₂ and Ni₂Zr compounds.

The partial radial distribution functions of Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} are shown in Figure 5.16. The coordination number of Ni-Ni, Ni-Zr, and Zr-Zr atomic pairs in the nearest neighbor shell are given in table 5.2. As discussed previously, the partial structure factors are sensitive to the composition. Therefore, the partial radial distribution functions are expected to be composition dependent. As shown in figure 5.16a, the magnitude of $RDF_{NiNi}(r)$ for Ni_{0.33}Zr_{0.67} is about 50% larger than that for Ni_{0.67}Zr_{0.33} whereas that of $RDF_{ZrZr}(r)$ for x = 0.33 is 30% to 50% lower than that for x = 0.67. The difference between the $RDF_{NiZr}(r)$ for the two compositions is about 30%. These results indicate that the local atomic number density depends strongly on the composition. From figure 5.16 one can see that the height of the first peak in the $RDF_{NiNi}(r)$ and $RDF_{ZrZr}(r)$ differs by about 50% between the two compositions while that in the $RDF_{NiZr}(r)$ changes by 30%. As a result, the nearest coordination numbers n_{NiNi} , n_{NiZr} , n_{ZrNi} and n_{ZrZr} vary, respectively, by about 56%, 36%, 62% and 35% with composition. Obviously, the local atomic environment of both Ni and Zr are very sensitive to composition. It is interesting to note, however, that the coordination distances (i.e. the peak positions of $RDF_{ij}(r)$ vary little with composition. As shown in table 5.2, the relative change of the coordination distances with composition is less than 2%.

There has been no previous report on the partial raidal distribution functions of amorphous Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33}². The atomic coordination numbers and inter-atomic distances of Ni_{0.33}Zr_{0.67}, however, have been evaluated by F. Paul *et al* using x-ray diffraction [49] and by R. Frahm *et al* [50] using EXAFS. Their results are listed also in table 5.2. In both of the studies, they were unable to obtain the structural parameters of the Ni-Ni pair. In reference [50], the inter-atomic distances were determined by a one-shell fit to the EXAFS spectrum based on Zr neighbors

²Reference [57] is entitled "Anomalous wide angle x-ray scattering of amorphous Ni₂Zr alloy", but in the text it said that the sample was a piece of ribbon used in reference [56] which is Ni_{0.63.7}Zr_{36.3}.



Figure 5.16: The partial radial distribution functions of $Ni_x Zr_{1-x}$, x = 0.33 and 0.67.

		Ni-	Ni	Ni-	Zr	Zr	Ni	Zr-	Zr	
Phase	\boldsymbol{x}	(r (Å)	N	r (\dot{A})	N	τ (Å)	N	r (Å)	N	Reference
a	0.33		<u> </u>	2.62	2.39	2.62	1.43	3.18	10.1	[50]
8	0.33			2.70	8.3	2.70	4.2	3.16	10.6	[49]
a	0.33	2.68	3.14	2.76	8.38	2.76	4.19	3.22	9.59	this work
с	0.33	2.63	2.00	2.74	8.00	2.74	4.00	•2.97	2.00	[105]
								*3.07	2.00	
								*3.39	8.00	
a	0.67	2.64	7.13	2.74	5.38	2.74	10.76	3.16	6.09	this work
c	0.67	2.45	6.00	2.87	ა.00	2.87	12.00	2.99	4.00	[105]

Table 5.3: The nearest neighbor coordination numbers of $Ni_x Zr_{1-x}$, x = 0.33 and 0.67.

a =amorphous; c = crystalline.

* Three different sites of Zr in the unit cell.

only. It can be seen from table 5.3, their inter-atomic distances for Ni-Zr and Zr-Zr pairs are generally 0.14Å smaller than those obtained in the present work. Our results show that up to 30% of the nearest neighbors about a Ni or Zr atom are Ni atoms. On the other hand, Ni atoms are 30% smaller than Zr atoms. Therefore, neglecting the Ni-Ni pair contribution leads to a underestimate of the inter-atomic distances of all the rest of the atomic paris. The coordination number of the Zr-Zr pair, n_{Zr-Zr} , which was evaluated in [50] agree with our result. However, the n_{NiZr} and n_{ZrNi} are significantly different from our results. As extensively discussed in the literature on the EXAFS investigation of amorphous alloys [50,106] this discrepancy is probably due to the non-Gaussian pair distribution functions which are difficult to investigate with EXAFS. In the study of Paul *et al* [49], only two x-ray diffraction experiments were carried out. The coordination numbers and inter-atomic distances of Ni-Zr, Zr-Ni, and Zr-Zr correlations were evaluated assuming the contribution of the Ni-Ni pair was small. It can be seen from table 5.3, the coordination numbers

presented in [49] agree with our results but the interatomic distances were under estimated because they neglected the Ni-Ni correlation.

From the above discussion, it is evident that sufficient and accurate structural parameters can only be obtained from complete evaluations of the partial radial distribution functions.

Though there is usually a discontinuity in the structure between amorphous and crystalline states, it is often helpful to compare the structures of the amorphous and the corresponding crystalline solids. In the next few paragraphs, the atomic structure of $Ni_{0.33}Zr_{0.67}$ and $Ni_{0.67}Zr_{0.33}$ metallic glasses are further analysed and compared to the crystalline NiZr₂ and Ni₂Zr phases.

For Ni_{0.33}Zr_{0.67}, there exists a stable intermetallic compound, NiZr₂ [61]. It has a body-centered tetragonal (BCT) structure ³. The coordination numbers and the inter-atomic distances in the unit cell of BCT NiZr₂ are listed in table 5.2. The distributions of three types of atomic pairs in BCT NiZr₂ are superimposed on the radial distribution functions of amorphous Ni_{0.33}Zr_{0.67} in figure 5.17. As one can see the distribution of the vertical bars are quite consistent with the $RDF_{ij}(r)$ curves. A Ni atom in the amorphous phase has 11 neighbors including 3 Ni atoms at 2.68Å and 8 Zr atoms at a further distance, 2.76Å. In crystalline NiZr₂ a Ni atom has 10 near veighbors comprising 2 Ni atoms at 2.63Å and 8 Zr atoms at 2.74Å. A Zr atom in Ni_{0.33}Zr_{0.67} has 14 neighbors including 4 Ni atoms at 2.76Å and 9.6 Zr atoms at 3.16Å, while a Zr atom in BCT NiZr₂ has 15 near neighbors comprising 4 Ni atoms at 2.74Å and 12 Zr atoms at three slightly different positions in the cell (see table 5.2). It is interesting that in the amorphous Ni_{0.33}Zr_{0.67} the inter-atomic distance of Ni-Ni is larger, but that of Zr-Zr is smaller than the corresponding distances in

³The compound NiHf₂ has the same structure as that of NiZr₂.



Figure 5.17: Comparison of the partial radial distribution functions of $Ni_{0.33}Zr_{0.67}$ and the local atomic structures of crystalline $NiZr_2$. The curves are the $RDF_{ij}(r)$ of $Ni_{0.33}Zr_{0.67}$ and the vertical bars represents the local atomic coordination numbers in crystalline $NiZr_2$.

crystalline Ni Zr_2 , while the Ni-Zr inter-atomic distance is about the same in the two phases. Nevertheless the local topological order is quite similar in amorphous Ni_{0.33} $Zr_{0.67}$ and in the crystalline compound Ni Zr_2 . In fact, in our DSC experiments amorphous Ni_{0.33} $Zr_{0.67}$ crystalizes directly into the equilibrium BCT Ni Zr_2 phase.

For Ni_{0.67}Zr_{0.33}, the crystalline Ni₂Zr phase is not indicated on the standard equilibrium binary phase diagram. An FCC structure of Ni₂Zr has been reported [105]. However, the crystallization product of amorphous Ni_{0.67}Zr_{0.33} is a bodycentered-orthorhombic peritectoid [66]. Unfortunately, the detailed structure of this phase is still unknown. Nevertheless, it is instructive to compare the amorphous Ni_{0.67}Zr_{0.33} to the FCC Ni₂Zr phase. The partial radial distribution functions of Ni_{0.67}Zr_{0.33} are compared to the local atomic structure of the FCC Ni₂Zr in figure 5.18. As can be seen from figure 5.17a, the distribution of Ni-Ni pair in amorphous Ni_{0.67}Zr_{0.33} looks quite similar to that in FCC Ni₂Zr. However, as shown in table 5.3, each Ni atom in the amorphous phase has 7 Ni neighbors at 2.64Å whereas a Ni atom in the crystalline phase has only 6 Ni neighbors at a much closer distance, 2.45Å. In figure 5.18b, it is found that the inter-atomic distances of Ni-Zr pairs in FCC Ni₂Zr correspond quite well to the maxima of the $RDF_{NiZ_{T}}(r)$ except in the first shell. As can be seen in table 5.3, the nearest neighbor coordination number n_{NiZr} is about the same in the two phases but the inter-atomic distance in amorphous Ni0.67Zr0.33 is 0.13Å smaller that that in FCC Ni₂Zr. Such a difference is also found for the Zr-Ni correlation. A Zr atom in the amorphous phase has about 11 Ni neighbors at 2.74Å and 6 Zr neighbors at 3.16Å. A Zr atom in the FCC phase, however, has 12 Ni neighbors at 2.87Å and only 4 Zr neighbors at 2.99Å. Though there are similarities between the atomic structure of amorphous Ni_{0.67}Zr_{0.33} and FCC Ni₂Zr, the similarities are not as strong as those between Ni0.33 Zro.67 and BCT NiZr2. This



Figure 5.18: Comparison of the partial radial distribution functions of $Ni_{0.67}Zr_{0.33}$ and the local atomic structures of crystalline Ni_2Zr . The curves are the $RDF_{ij}(r)$ of $Ni_{0.67}Zr_{0.33}$ and the verticle bars represents the local atomic coordination numbers in crystalline Ni_2Zr .

is consistent with the fact that the crystallization product of amorphous $Ni_{0.67}Zr_{0.33}$ is not the FCC Ni_2Zr phase but a body-centered orthorhombic peritectoid whose detailed structure has yet to be worked out [66].

5.4 The chemical short-range order in Ni-Zr glasses5.4.1 The Bhatia-Thornton representation

As discussed in chapter 2, the Bhatia-Thornton partial structure factors, $S_{nn}(Q)$, $S_{nc}(Q)$, and $S_{cc}(Q)$ are useful for examining the chemical short-range order in amorphous materials. The $S_{nn}(Q)$ and $S_{cc}(Q)$ correspond to the mean square fluctuations in the number density and concentration, respectively, and $S_{nc}(Q)$ denotes the cross term between these two fluctuations. The $S_{nn}(Q)$, $S_{nc}(Q)$ and $S_{cc}(Q)$ for Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} are obtained by a linear transformation of the Faber-Ziman partial structure factors using relations 2.48, 2.49 and 2.49. Each of these Bhatia-Thornton partial structure factors and the corresponding correlation functions are discussed bellow.

i. $S_{nn}(Q)$: The number-number structure factor describes the topological short range order in the amorphous materials. It reflects the local atomic configuration irrespective of the type of atom. Therefore, $S_{nn}(Q)$ is expected to look similar to the total structure factor S(Q). Figure 5.19 and 5.20 show this feature of $S_{nn}(Q)$ for Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} glasses. $S_{nn}(Q)$ varies with composition. As shown in figure 5.21a, the $S_{nn}(Q)$ for Ni_{0.33}Zr_{0.67} has lower amplitude than that for Ni_{0.67}Zr_{0.33}. This means that the number density fluctuation is relatively weaker in the Zr-rich sample.



Figure 5.19: The number-number structure factor comparing to the total structure factor for $Ni_{0.33}Zr_{0.67}$.



Figure 5.20: The number-number structure factor comparing to the total structure factor for $Ni_{0.67}Zr_{0.33}$.



Figure 5.21: The Bhatia-Thornton partial structure factors of $Ni_{0.33}Zr_{0.67}$ and $Ni_{0.67}Zr_{0.33}$. The solid lines are the $S_{n,c}(Q)$ for x = 0.33 obtained using the isomorphous method while the dashed lines are that obtained using combined x-ray and neutron diffraction. The dotted lines are the $S_{n,c}(Q)$ for x = 0.67.

The Fourier transform of $S_{nn}(Q)$ gives the number-number pair distribution function, $\rho_{nn}(r)$, which is related to the partial atomic pair distribution functions by:

$$\rho_{nn}(r) = c_1 \rho_{11}(r) + c_2 \rho_{22}(r) + \rho_{12}(r)$$
$$= c_1 \rho_1(r) + c_2 \rho_2(r)$$

where $\rho_i(r) = \sum_j \rho_{ij}(r)$. Figure 5.22a shows the reduced number-number correlation function $G_{nn}(r) = 4\pi r \rho_{nn}(r)$ for both compositions ⁴. The first peak of the $G_{nn}(r)$ for x = 0.33 is relatively broad with the maximum at 3.12Å. There is a very pronounced shoulder at low r side. It shows the contribution of the number density around Ni, the small atoms. This contribution becomes very strong for x = 0.67shown by the low r position of the first peak, $r \sim 2.66$ Å, and the large amplitude of the $G_{nn}(r)$ for Ni_{0.67}Zr_{0.33}. These characteristics reflect the predominance of small atoms in the number density in the Ni-Zr glasses.

ii. $S_{nc}(Q)$: The number-concentration structure factor describes the correlation between density and concentration fluctuations. The oscillations of $S_{nc}(Q)$ around zero reflects the size effect between the two types of atoms. As shown in figure 5.21b, in spite of the large difference in the atomic size of the two constituent atoms, the amplitude of the $S_{nc}(Q)$ (dotted line) for the Ni-rich alloy remains low. This indicates less size effect in the Ni-rich sample. For the Zr-rich alloy, however, a stronger size effect is revealed by the large amplitude of the corresponding $S_{nc}(Q)$ (solid line).

The Fourier transform $\rho_{nc}(r)$ of $S_{nc}(Q)$ is a measure of the difference in the ⁴In the literature, the discussion is usually carried out in terms of the reduced correlation functions. Therefore, in figure 5.22 the $G_{n,c}(r)$, rather than the $\rho_{n,c}(r)$ are presented. atomic distribution function of two types of atoms:

$$\rho_{nc}(r) = c_1 c_2 [\rho_1(r) - \rho_2(r)]$$
(5.1)

The reduced number-concentration correlation function $G_{nc}(r) = 4\pi r \rho_{nc}(r)$ for both compositions is shown in figure 5.22b. The two curves are relatively in phase, but the Zr-rich sample has higher first positive and negative peaks. It indicates that the density fluctuation in Ni-Zr glasses increases with the concentration of Zr (the big atoms). Furthermore, the position of the first positive peak ($r \sim 2.7 \text{\AA}$) and the first negative peak ($r \sim 3.2 \text{\AA}$) seems to be independent of composition. This means that in Ni-Zr glasses the number density around Ni atoms at 2.7 Å is always higher than that around Zr atoms, and the opposite situation occurs at $r \sim 3.2 \text{\AA}$.

iii. $S_{cc}(Q)$: The concentration-concentration structure factor oscillates about c_1c_2 , where c_1 and c_2 are the concentrations of the two constituents. Figure 5.21c shows the $S_{cc}(Q)/c_1c_2$ for both Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33}. The first peak of the $S_{cc}(Q)$ for x = 0.33 is positive at $Q = 2.4 \text{\AA}^{-1}$ while that for x = 0.67 also has a positive first peak but it appears at a much lower position, $Q = 1.7 \text{\AA}^{-1}$. A peak at $Q \leq 2 \text{\AA}^{-1}$ is usually called pre-peak. The pre-peak is often considered as an indication of strong chemical short-range order in amorphous materials. This can be misleading. Further discussion on the relationship between the pre-peak and the chemical short-range order will be given section 5.4.2.

The Fourier transform of $S_{cc}(Q)$ yields the concentration-concentration correlation function, $\rho_{cc}(r)$, which tells how much the local chemical composition differs from the average composition. The positive peaks of the $G_{cc}(r)$ correspond to the clustering of one type of atom while negative peaks show the tendency towards segregation between unlike atoms. Figure 5.22c shows the reduced concentration-



Figure 5.22: The number-concentration correlation functions of Ni_xZr_{1-x} , x = 0.33 and 0.67.

concentration correlation function $G_{cc}(r) = 4\pi r \rho_{cc}(r)$ for Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33}. The two curves have inverted maxima and minima. It is clear that, for both compositions, the intensities of the positive peaks of $G_{cc}(r)$ balance those of the negative peaks. This means that the local clustering effect of Ni or Zr atoms is cancelled out by the segregation tendency between Ni and Zr atoms. This is evidence of small chemical short range ordering in the Ni-Zr glasses. Indeed, the chemical short range order parameter α_1 (equation 2.55) for both the compositions is found to be small in comparison with that of other Ni containing metallic glasses (see table 5.3). Ni-Zr glasses are therefore a quite random mixture of Ni and Zr.

Table 5.3: The chemical shor range order parameter of amorphous Ni-Zr compared with other Ni containing glasses.

glass	Ni _{0.81} B _{0.19}	$\mathrm{Ni}_{0.8}\mathrm{P}_{0.2}$	Ni _{0.4} Ti _{0.6}	Ni _{0.33} Y _{0.67}	$Ni_{0.33}Zr_{0.67}$	Ni _{0.67} Zr _{0.33}
α_1	-0.21	-0.23	-0.2	-0.15	-0.024	-0.047
ref.	[103]	[107]	[36]	[38]	This work	This work

5.4.2 Relationship between the "pre-peak" and the chemical short-range order

It should be noted that the $S_{cc}(Q)$ of Ni_{0.67}Zr_{0.33} has a pronounced pre-peak at $Q = 1.7\dot{A}^{-1}$. The $S_{cc}(Q)$ of Ni_{0.33}Zr_{0.67}, however, has a first peak centered at $Q = 2.45\dot{A}^{-1}$. Based on the difference between the $S_{cc}(Q)$ of Ni_{0.33}Zr_{0.67} and that of Ni_{0.67}Zr_{0.33}, the relationship between the "pre-peak" and the chemical short range ordering in amorphous materials is now discussed.

As indicated in chapter 4, for many metallic glasses, a pre-peak is often observed in the neutron diffraction pattern which is absent in the x-ray curves [33,102104,108]. Sometimes, a weak pre-peak appears in the x-ray pattern and becomes the main peak in the neutron pattern [30,109]. In the literature, the presence of a pre-peak is often attributed to chemical shor-range ordering in the material. This is probably because of the following:

- Only the partial structure factor $S_{cc}(Q)$ may have the first peak at $Q < 2\dot{A}^{-1}$;
- $S_{cc}(Q)$ represents the chemical short-range ordering in the material;
- The weighting factor w_{nn} for neutron diffraction is sometimes larger than that for x-ray diffraction. When the neutron experiment is performed on a zero alloy, the total structure factor is identical to the quantity $S_{cc}(Q)$.

However, as indicated in reference [110] (1983), difficulties arise with the original Bhatia-Thornton formalism in the interpretation of the structure factor of $Ni_{60}Nb_{40}$. For this system, a pre-peak is observed only in the neutron pattern, but the weighting factor w_{cc} for neutron diffraction is 60% smaller than that for x-rays. Unfortunately, this work seems to be ignored in subsequent structural studies of metallic glasses in which a pre-peak observed in the neutron diffraction pattern is still simply explained as an indication of chemical short range ordering without giving any further evidence.

In this work, the neutron diffraction patterns of Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33} both show a pre-peak which is absent in the x-ray patterns of the corresponding Ni-Zr or Ni-Hf samples. However, as listed in table 5.5, the neutron weighting factor w_{cc} is, in some cases, much smaller than that of x-rays. The peak position is about the same for the two compositions ($Q = 1.75 \text{\AA}^{-1}$) but the intensity of Ni_{0.33}Zr_{0.67} is 10% lower than that of Ni_{0.67}Zr_{0.33}.

For Ni_{0.33}Zr_{0.67}, as shown in figure 5.21c, the $S_{cc}(Q)$ deduced from x-ray and neutron diffraction data (dashed line) shows no pre-peak neither does that deduced from

measurement	sample	w_{nn}	wnc	w_{cc}
x-ray	Ni _{0.33} Zr _{0.67}	0.9784	-0.6017	0.0216
••	$\mathrm{Ni}_{0.33}\mathrm{Hf}_{0.67}$	0.8875	-1.3289	0.1125
neutron	Ni _{0.33} Zr _{0.67}	0.9685	0.7411	0.0315
x-ray	Ni _{0.67} Zr _{0.33}	0.9730	-0.6686	0.0270
••	Ni _{0.67} Hf _{0.33}	0.8154	-1.6334	0.1846
neutron	Ni _{0.67} Zr _{0.33}	0.9750	0.3309	0.0250

Table 5.4: Bhatia-Thornton weighting factors for $Ni_{0.33}Zr_{0.67}$ and $Ni_{0.67}Zr_{0.33}$. The data for x-ray experiments are given at $Q = 0.0 \text{\AA}^{-1}$

from the x-ray isomorphous substitution data (solid line). On the other hand, the $S_{cc}(Q)$ of Ni_{0.67}Zr_{0.33} (dotted line), which is obtained from x-ray and neutron diffraction data, has a strong peak at $Q = 1.7 \text{\AA}^{-1}$. Although the origin of the pre-peak in the neutron pattern of Ni_{0.33}Zr_{0.67} is still unknown ⁵, it is evident that the pre-peak is not necessarily a consequence of the modulations of the concentration fluctuation term $S_{cc}(Q)$. The chemical short range ordering in the material should only be examined with the $S_{cc}(Q)$ itself and its Fourier transform, the concentration fluctuation correlation function $\rho_{cc}(r)$.

⁵The ratio of Ni and Zr scattering amplitudes is much smaller for x-rays than for neutrons. Therefore, it seems to be possible that the pre-peak which was only observed in neutron diffraction is caused by the correlation between Ni-Ni atoms. This is, however, inconsistent with the results presented in sections 5.3, 5.4.1.

Chapter 6 Conclusions

This thesis presents a structural study of Ni-Zr metallic glasses. It is the first time that a careful and systematic investigation into the structure of a glassy metallic system has been carried out. The results have improved our understanding of the structure of metallic glasses and clarified confusion in previous studies.

The amorphous alloys Ni_xZr_{1-x} , $0.25 \le x \le 0.86$, were prepared using both melt-spinning and sputtering. The total structure factors of these alloys were obtained from x-ray and neutron diffraction, as well as anomalous x-ray scattering. We selected two compositions, $Ni_{0.33}Zr_{0.67}$ and $Ni_{0.67}Zr_{0.33}$, for a detailed study of the partial structure factors. Isomorphous substitution (partially or totally replacing Zr with Hf) and combined x-ray and neutron diffraction were employed to obtain these partial structure factors.

We used both high-angle fitting and the KMN method together to normalize the diffraction data. The resulting total structure factors have the accuracy of 1-4%. We also obtained the total radial distribution functions and the nearest neighbor coordination numbers from the total structure factors. Our results show that these quantities for Ni-Zr glasses have strong composition dependence. A structural turning point is found at Ni concentration of ~ 0.45 . This characteristic is in good

Chapter 6. Conclusions

agreement with the composition dependence of the electrical resistivity and thermoelectric power of Ni-Zr glasses. It suggests a close relationship between the near neighbor atomic structure and the electron transport properties of these alloys.

Based on our studies of the total structure factor, the total radial distribution function, and the crystallization enthalpy in the whole range of composition, we have shown that there is no difference between the atomic structure of melt-spun and sputtered Ni-Zr glasses.

We obtained two independent sets of Faber-Ziamn partial structure factors for Ni_{0.33}Zr_{0.67} from seven independent isomorphous substitution measurements and combined x-ray and neutron diffraction experiments. The two sets of results are in agreement and the overall uncertainties of these partial structure factors is less than 4%. Our study confirmed the relability of the isomorphous substitution method in evaluating the partial structure factors of Ni-Zr(Hf) glasses. The Faber-Ziman partial structure factors of Ni_{0.67}Zr_{0.33} were obtained using combined x-ray and neutron diffraction with an accuracy better than 4%. The Faber-Ziamn partial structure factors are found to be strongly compositional dependent. Therefore, it is inappropriate to use the concentration technique to evaluate the partial structure factors of metallic glasses. The partial radial distribution functions were evaluated for Ni_{0.33}Zr_{0.67} and Ni_{0.67}Zr_{0.33}. The results gave us a complete insight into the local atomic structure of these metallic glasses. The local topological order in amorphous $Ni_{0.33}Zr_{0.67}$ is found to be quite similar to that in crystalline compound NiZr₂. Unfortunatly the structure of crystalline Ni₂Zr has not been completely worked out, therefore, a similar comparison cannot be made for the Ni_{0.67}Zr_{0.33} alloy.

We have also discussed the chemical short-range order in the Ni-Zr glasses in terms of the Bhatia-Thorton partial structure factors. Our results show that, compared to other Ni containing metallic glasses, a relatively random mixture is retained in Ni-Zr glassy system. It is shown that the pre-peak observed in the neutron diffraction pattern of metallic glasses in not necessarily due to the modulations of the Bhatia-Thornton concentration fluctuation term $S_{cc}(Q)$. Our results reveal no correlation between the pre-peak and chemical short range-order in Ni-Zr glasses. Therefore, the chemical short-range ordering in amorphous materials should only be examined with $S_{cc}(Q)$ and the concentration-concentration correlation function $\rho_{cc}(r)$.

Suggestions for further research

Further studies should be carried out using the Reversible Monte-Carlo (RMC) simulation to model the atomic structure of Ni-Zr glasses. The RMC modeling could be used to extract the three dimentional information from our precisely measured partial structure factors and provide further structural information, for example, the physical configuration and the bond angle distribution in the Ni-Zr metallic glasses. The accurate Faber-Ziman partial structure factors determined in this work could also be used to calculate the electrical resistivity and thermoelectric power of Ni-Zr metallic glasses and to examine the validity of the Faber-Ziman model.

The mathematics in the evaluation of the partial structure factors

In principle, the partial structure factors can be evaluated from three independent measurements by solving the linear equations:

$$\mathbf{T}(Q) = \mathbf{W}(Q)\mathbf{P}(Q) \tag{7.1}$$

where T(Q) is the vector of total structure factors:

$$\mathbf{T}(Q) = \begin{bmatrix} S_1(Q) - 1 \\ S_2(Q) - 1 \\ S_3(Q) - 1 \end{bmatrix}$$
(7.2)

 $\mathbf{P}(Q)$ is the vector of the partial structure factors:

$$P(Q) = \begin{bmatrix} S_{ii}(Q) - 1 \\ S_{ij}(Q) - 1 \\ S_{jj}(Q) - 1 \end{bmatrix}$$
(7.3)

and W(Q) is the matrix of the weighting factors:

$$W(Q) = \begin{bmatrix} w_{ii}^{1} & w_{ij}^{1} & w_{jj}^{1} \\ w_{ii}^{2} & w_{ij}^{2} & w_{jj}^{2} \\ w_{ii}^{3} & w_{ij}^{3} & w_{jj}^{3} \end{bmatrix}$$
(7.4)

A unique solution is found if the determinant of W(Q) is different from zero, i.e. if the three equations are linearly independent. Mathematically, the conditioning of

a weighting factor matrix can be measured by the normalized determinant of the weighting matrix:

$$|\mathbf{W}_{n}(Q)| = |W_{ij}(Q)/\{\sum_{j} [W_{ij}(Q)]^{2}\}^{1/2}|$$
(7.5)

A well-conditioned set of equations yield $|W_n(Q)|$ of order ± 1 . It can be shown that, for the metallic glasses whose three partial structure factors have been evaluated so far, $|W_n(Q)|$ is normally very samll $(10^{-2} - 10^{-4})^{-1}$, i.e. the set of equations (equation 7.1) is ill-conditioned.

Depending on the conditioning of the matrix W(Q) the solution of equation 7.1 may be obtained using one of the following methods:

1. The direct solution

$$\mathbf{P}_o(Q) = \mathbf{W}^{-1}(Q)\mathbf{T}(Q) \tag{7.6}$$

2. The least square evaluation

$$\widehat{\mathbf{P}}(Q) = [\mathbf{W}'(Q)\mathbf{W}(Q)]^{-1}\mathbf{W}'(Q)\mathbf{T}(Q)$$
(7.7)

3. The "ridge regression" evaluation

$$\mathbf{P}^{*}(Q) = [\mathbf{W}'(Q)\mathbf{W}(Q) + \alpha \mathbf{I}]^{-1}\mathbf{W}'(Q)\mathbf{T}(Q)$$
(7.8)

where W'(Q) and $W(Q)^{-1}$ are, respectively, the transpose and inverse of the matrix W(Q). The parameter α in equation 7.8 is an arbitrary number which will be disscused later.

When W(Q) is ill-conditioned, the elements of the matrix W^{-1} are often very large numbers. Therefore, in equation 7.6, the errors in the total structure factor

¹Wagner has given the values of $|\mathbf{W}_n(Q)|$ for some previous studies in his review paper in reference [5].

vector T(Q) are greatly amplified. As a consequence, the results given by $P_o(Q)$ is usually physically meaningless.

The least-square solution 7.7 is a biased estimate of 7.1. It has been proved mathematically, that for ill-conditioned data, (e.g. $|W_n(Q)| \sim 10^{-4}$) the least-square estimate is expected to be a very poor representation of the true vector P(Q) in equation 7.1 [100,101]. Therefore, the accuracy of the least-square solution must be examined with additional experiments.)

Strictly speaking, there always exist some uncertainties in the experimental data. Therefore, the partial structure factors should be evaluated from

$$\mathbf{T}(Q) = \mathbf{W}(Q)\mathbf{P}(Q) + \mathbf{E}(Q)$$
(7.9)

where E(Q) is the error in the vector T(Q). Equation 7.9 is a typical problem for which the solution can be obtained using ridge regression analysis [100,101]. Let $P^{*}(Q)$ in equation 7.8 be the solution of 7.9, the error in vector T(Q) is then given by

$$\mathbf{E}^{\bullet}(Q) = \mathbf{T}(Q) - \mathbf{W}(Q)\mathbf{P}^{\bullet}(Q)$$
(7.10)

and the variance in $\mathbf{P}^{*}(Q)$ is given by

$$\mathbf{V}(Q) = [\mathbf{W}'(Q)\mathbf{W}(Q) + \alpha \mathbf{I}]^{-1}[\mathbf{W}'(Q)\mathbf{W}(Q)][\mathbf{W}\mathbf{a}'(Q)\mathbf{W}(Q) + \alpha \mathbf{I}]^{-1}\sigma^{2}\mathbf{I}_{o} \quad (7.11)$$

where σ is the statistical error in the total structure factors and I_{σ} is the identity vector. Therefore, the total error in P(Q) is given by

$$\varepsilon(Q) = \mathbf{E}^{\bullet}(Q)\mathbf{E}^{\bullet}(Q) + Tr[\mathbf{V}(Q)]$$
(7.12)

where $Tr[\mathbf{V}(Q)]$ is the trace of $\mathbf{V}(Q)$. It has proved that there exists a $\alpha > 0$ (typically 10^{-4} to 1) such that the errors in $\mathbf{P}(Q)$, $\varepsilon(Q)$, are minimized.

It can be shown that the ridge analysis solutions are the linear combinations of the ordinary solutions $P_o(Q)$:

$$\mathbf{P}^{\bullet}(Q) = [\mathbf{W}(Q)^{t}\mathbf{W}(Q) + \alpha \mathbf{I}]^{-1}[\mathbf{W}(Q)^{t}\mathbf{W}(Q)]\mathbf{P}_{o}(Q) = \mathbf{Z}(Q)\mathbf{P}_{o}(Q)$$
(7.13)

With ill-conditioned data, off-diagonal elements of Z(Q) are found *not* negligible. This means that the ridge analysis solutions $P^{\bullet}(Q)$ are the linear combinations of $P_{o}(Q)$. Since the ridge regression results are biased estimate of the true partial structure factors, is it necessary to renormalize the matrix Y(Q), such that

$$Y_{ij}^{*}(Q) = \frac{Y_{ij}(Q)}{\sum_{j} Y_{ij}(Q)}$$
(7.14)

This renormalization is equivalent to the physical constraint that $S_{ij}(Q) \rightarrow 1 \text{ as } Q \rightarrow \infty$ [35]. The solution of equation 7.8 is finally given by

$$\mathbf{P}^{\bullet}(Q) = \mathbf{Y}^{\bullet}(Q)\mathbf{T}(Q) \tag{7.15}$$

and the incertainty in the partial structure factor vector P(Q) can be estimated by:

$$\Delta \mathbf{P}(Q) = \sigma^2 [\mathbf{Y}^*(Q) \mathbf{Y}^{*\prime}(Q)]$$
(7.16)

The ridge analysis has been used by Wagner and his coworker to evaluate the partial structure factors of metallic glasses [35,111]. In practice, it is desirable to examine the ridge solution for a range of admissible values of α with physical constraints and additional experimental data. The computer program using the ridge analysis to evaluate the Faber-Ziman partial structure factors in this work is available from the auther on request.

Appendix B

Feasibility study using anomalous x-ray scattering.

Anomalous x-ray scattering experiments were performed at the F3 beam station of Cornell High Energy Synchrotron Source (CHESS) Laboratory, Ithaca, New York, U. S. A. The experimental arrangement is shown in figure B1. The intense white radiation from the storage ring was monochromatized by a pair of Si(111) single crystals. The intrinsic bandpass of this monochromator assembly is $\Delta E/E = 1.3 \times$ 10^{-4} . The curvature of the reflection planes of these crystals can be changed so that the incident beam energy can be adjusted. A Zr-foil was used to calibrate the primary beam energy. The foil was $25\mu m$ thick and the absorption edge is

$$E_{K} = 17.998 keV$$

An ich chamber was placed after the source slit to monitor the incident beam intensity.

The samples were the same as those used for the 2θ scanning x-ray diffraction experiments. They were mounted on a Huber four axis diffractometer. The ω and 2θ goniometers were aligned using a pin mounted at the center of the diffractometer. The experiments were performed in symmetrical transmission geometry. As shown in figure 7, the transmittance of the sample was recorded using an ion chamber at $2\theta = 0^{\circ}$ while the scattering intensity was measured with a phototube, scintillation detector.

Appendix B



Figure B1: A schematic diagram of the setup used in the anomalous z-ray scattering experiments.

The experiments were carried out at at several energies around the K-absorption edge of Zr. The energies were 17.45, 17.50, 17.675, 17.80, 17.90, 17.95, 17.975, 17.99, and 18.00keV. The software used to collect the diffraction data was similar to that used in the conventional x-ray diffraction experiments. For $5^{\circ} \leq 2\theta \leq 60^{\circ}$, a stepwidth of 0.2° was used, for $60^{\circ} \leq 2\theta \leq 120^{\circ}$, a stepwidth of 2.0° was used. Since the storage ring is filled at about 60 minute intervals, each measurement $(5^{\circ} \leq 2\theta \leq 120^{\circ})$ was done in about 50 min.

The data reduction for the anomalous x-ray scattering experiments is similar to that for the conventional x-ray diffraction measurements (see chapter 2). The total structure factor of $Ni_{0.33}Zr_{0.67}$ was obtained for several energies around the K-edge of zirconium. However, these results were not used in this research for two reasons:

- The subtraction of the Compton scattering intensity C(Q) from the raw data
 Iobs often causes large uncertainties because, at large values of Q, C(Q) can
 be as high or higher than the coherent scattering intensity. As shown in figure
 4.3, C(Q) can be effectively eliminated by a diffracted beam monochromator.
 However, because of the space limit inside the F3 hut at CHESS, we could not
 use an analyzer crystal in the diffracted beam²;
- 2. The incident beam fluctuates because of the natural decay of the current in the storage ring. Although an electronic feedback system was used to compensate the ring current fluctuation, the measured intensity curves were not reproducible.

The motivation of performing the anomalous x-ray diffraction experiments is to obtain reliable partial structure factors independent of the evaluations using x-ray

²The 2θ axis is horizontal. When an analyser crystal was mounted in the diffracted beam, the position of the detector was limited to $2\theta < 50^{\circ}$ before the 2θ arm hit the ceiling.
Appendix **B**

isomorphous substitution or combinations of x-ray and neutron diffraction. Unfortunately, this could not be realized in this work. Nevertheless, it was worthwhile learning about the anomalous x-ray scattering technique. With x-rays of 17.5keV and 17.95 keV, one could obtain the total structure factors with a contrast as high as 20%. It is believed that, given more beam time, one could overcome the present experimental difficulties and obtain accurate partial structure factors of Ni-Zr glasses from the anomalous x-ray scattering measurements.

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