

Modelling the structure of Ni₆₅B₃₅ metallic glass by reverse Monte Carlo simulation

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1993 J. Phys.: Condens. Matter 5 8815

(<http://iopscience.iop.org/0953-8984/5/47/007>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 11/05/2010 at 02:16

Please note that [terms and conditions apply](#).

Modelling the structure of $\text{Ni}_{65}\text{B}_{35}$ metallic glass by reverse Monte Carlo simulation

László Pusztai† and Erzsébet Sváb‡

† Laboratory of Theoretical Chemistry, L. Eötvös University, Budapest 112, POB 32, H-1518, Hungary

‡ Research Institute of Solid State Physics, Hungarian Academy of Sciences, Budapest, POB 49, H-1525, Hungary

Received 22 June 1993, in final form 26 August 1993

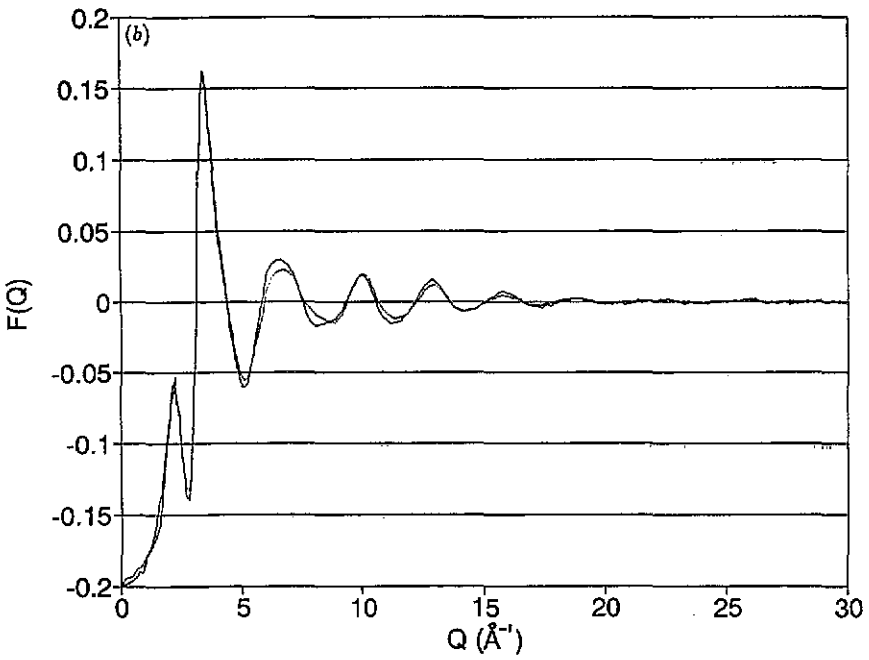
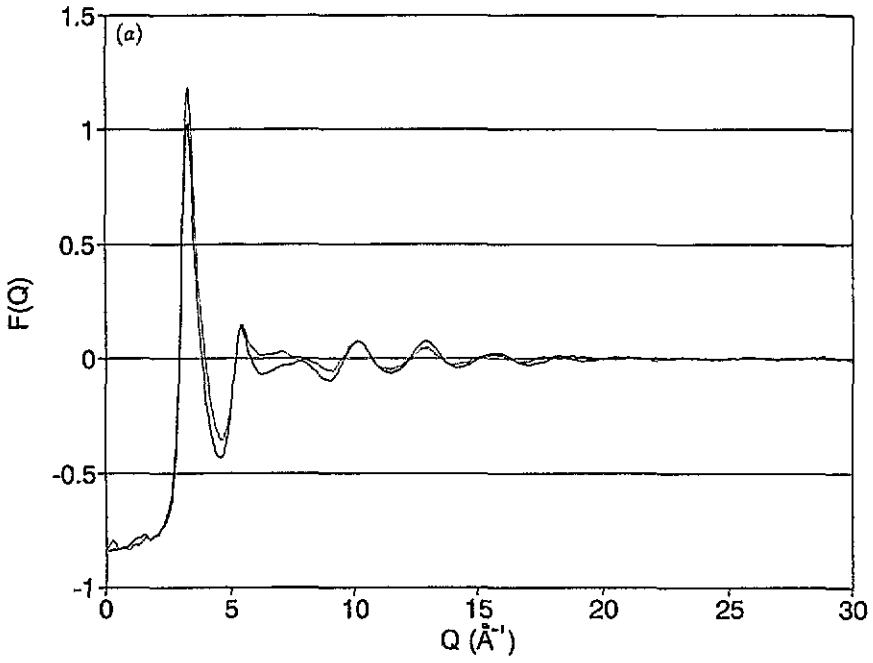
Abstract. Reverse Monte Carlo (RMC) simulation was applied for modelling the atomic level structure of the $\text{Ni}_{65}\text{B}_{35}$ amorphous metallic alloy. Three experimental total structure factors from isotopic substitution neutron diffraction measurements were used as input data. Using the particle configurations that were provided by the RMC calculations, neighbour distribution functions and cosine distribution of bond angles were evaluated. Local symmetries were found to be well defined around Ni atoms. B atoms are distributed more randomly. Using constraints on the B–B coordination number it is shown that the presence of boron pairs or the formation of boron chains are possibilities. None of these implications changed the local structure considerably, although we could not fully impose the constraints, because the level of RMC fit would have deteriorated.

1. Introduction

There is a wide range of structural models which try to speculate about the possible local arrangements of particles in the glassy state [1–3]. Some of them consider the possibility of constructing ‘prototype’ structures, in terms of either pair correlation functions [2] or quasi-crystalline clusters [3]. Computer-built models using simple rules, such as the exclusion of direct contact between particles of smaller concentration, are also in use [1]. It is notable that simple dense packing models applied, for instance, in [1], can result in a relatively high level of accuracy. This finding reflects the fact that at extremely large number densities excluded volume effects play an important role in determining basic structural features.

In this work reverse Monte Carlo (RMC) simulation [4–6], a method for structural modelling based directly on experimental data is used for investigating the local structure of $\text{Ni}_{65}\text{B}_{35}$. This technique is similar to the standard (metropolis) Monte Carlo simulation [7], the main difference being that instead of minimizing configurational energy it moves particles around in order to achieve the best agreement available with an experimental structure factor or radial distribution function. In equilibrium therefore one obtains sets of particle coordinates (‘configurations’) that are consistent with the original diffraction data.

In the rapidly growing family of amorphous metallic alloys $\text{Ni}_x\text{B}_{100-x}$ materials are amongst the most exhaustively studied. Several neutron diffraction studies with isotopic substitution were carried out on these glasses [1,8–10]. In the current work the most recent study on $\text{Ni}_{65}\text{B}_{35}^8$ was used as input for RMC. One of the specific properties of this glass is its high boron content, and as a consequence of this a B–B contact was found here [8], as well as in an earlier measurement on $\text{Ni}_{64}\text{B}_{36}^9$. As an uncertain feature it was also reported for $\text{Ni}_{81}\text{B}_{19}^1$, and a very recent RMC study on it [11] did not exclude the possibility of the



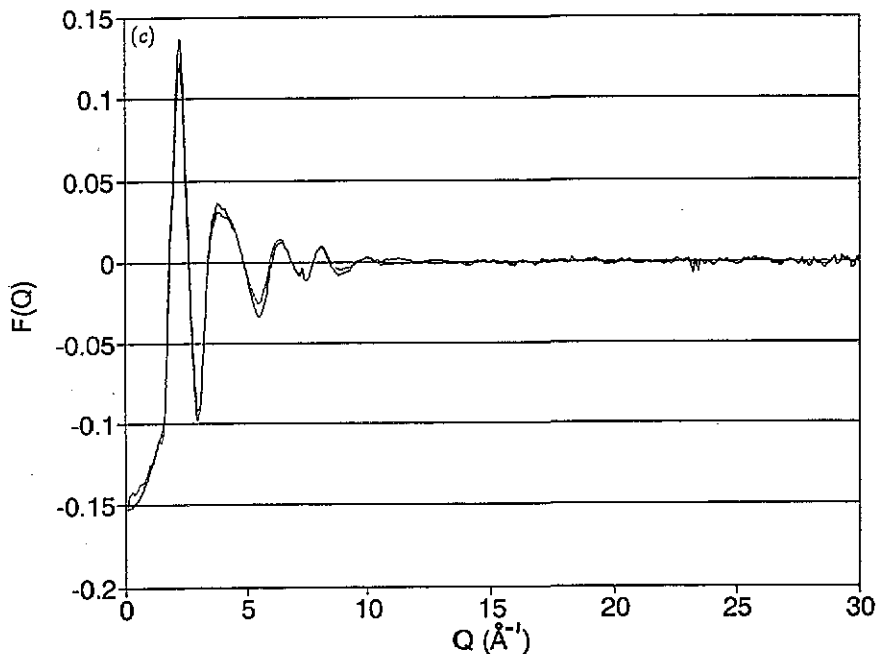


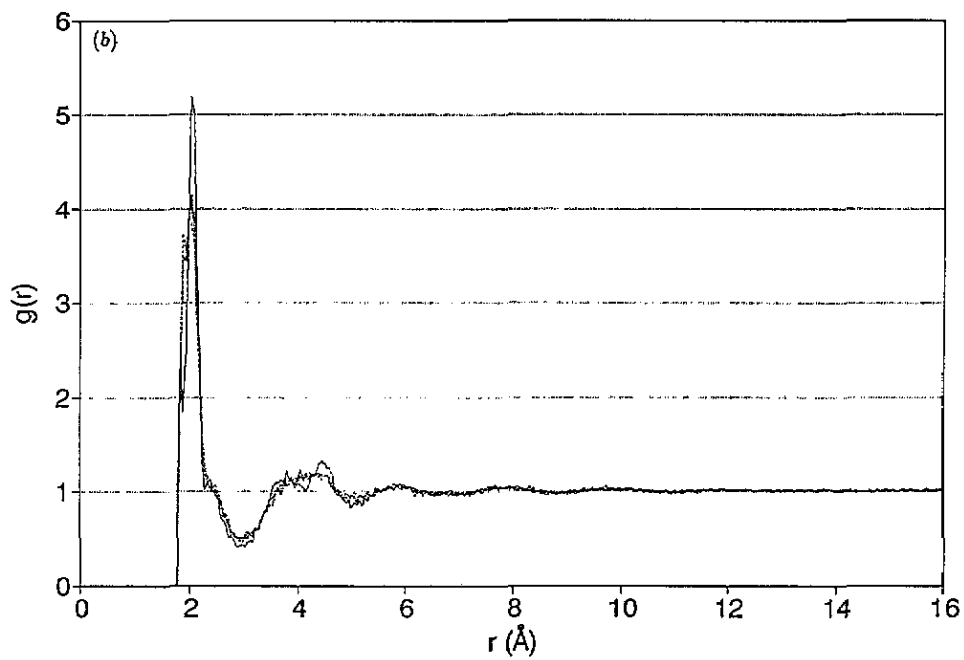
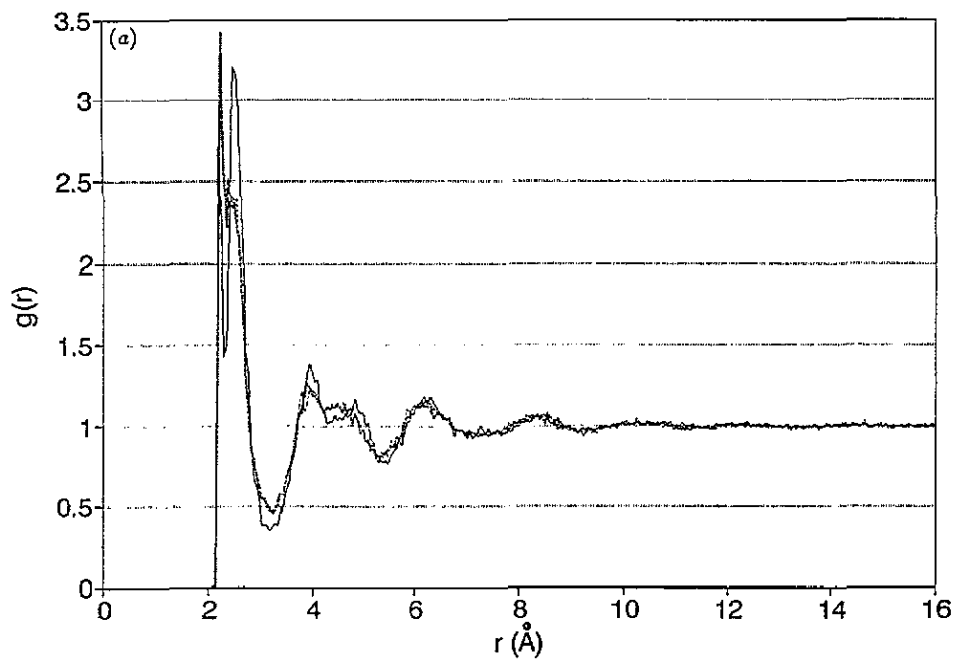
Figure 1. RMC fits (dots) of experimental values of $F(Q)$ (full curve). (a) Ni isotopes of natural abundance; (b) ^{60}Ni ; (c) ^{0}Ni (see [8]). Dotted curves also denote fits from run 2 and run 3 (see text).

contact. There was an attempt at fitting a mixture of crystalline structures to experimental data [3], but only a very small proportion of the experimental information was used there.

The aim of this study was to give a structural model for amorphous metallic $\text{Ni}_{65}\text{B}_{35}$ that would be consistent with the available diffraction data. Two distinct models for the relative spatial arrangement of the boron atoms were proposed on the grounds of Mössbauer experiments on Fe-B metallic glasses [12]. One is the existence of well defined boron pairs, while the other assumes the existence of longer boron chains. Both models are consistent with the average number of B atoms in the first neighbour shell of boron atoms which was experimentally found to be about one [8]. These assumptions can be checked by using constraints on the B-B coordination number during the calculations. In this way consistency with the constraints and with the data at the same time is required. From the particle coordinates quantities characteristic to local ordering were calculated. In the next sections details and results of these computations will be given.

2. Calculation details

Reverse Monte Carlo simulations for systems containing 4096 particles were carried out, using experimental total coherent scattering functions, $F(Q)$ (see e.g. [6]), as input. Of the particles, 2664 were assigned as Ni atoms. The experimental number density of $\rho = 0.112 \text{ \AA}^{-3}$ was applied, resulting in a boxlength of $L = 33.2 \text{ \AA}$. Distances of closest approaches between atoms of type α and β , $\Delta_{\alpha\beta}$, were applied in order to speed up calculations. The values $\Delta_{\text{NiNi}} = 2.1 \text{ \AA}$, $\Delta_{\text{NiB}} = 1.8 \text{ \AA}$ and $\Delta_{\text{BB}} = 1.6 \text{ \AA}$ were derived from previous experimental studies [1,8,9].



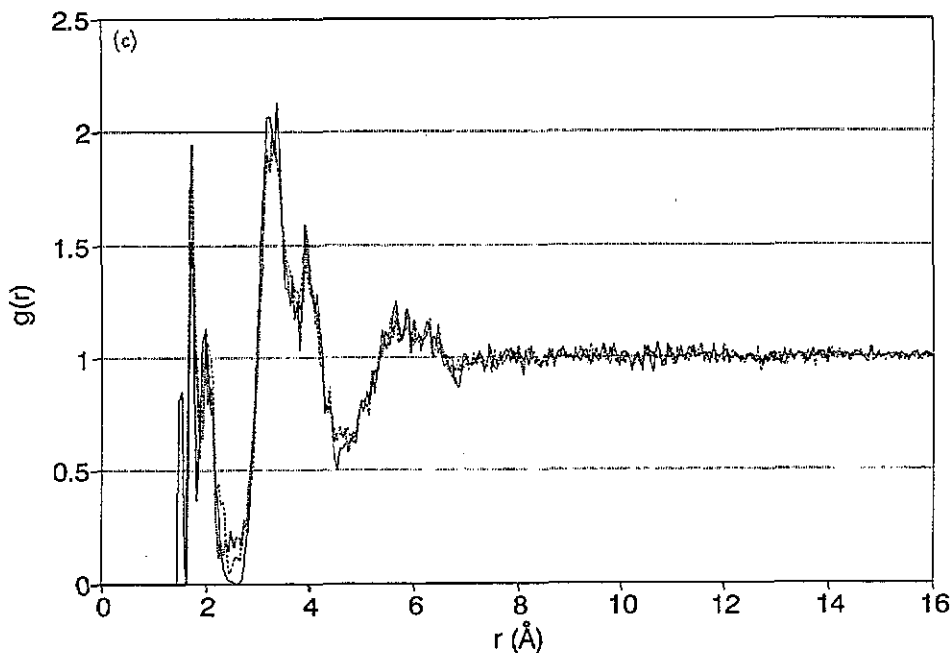


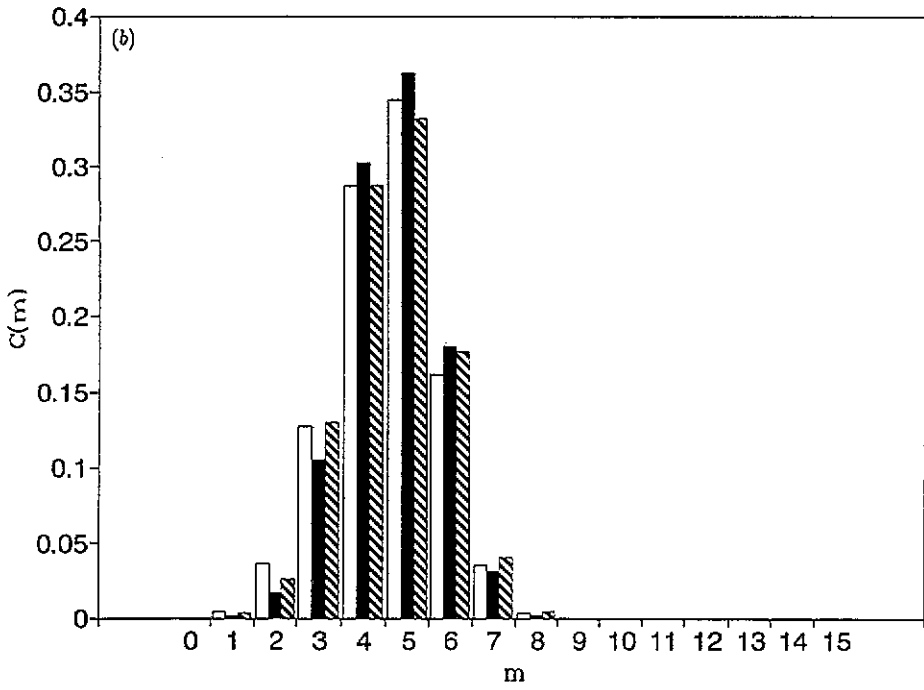
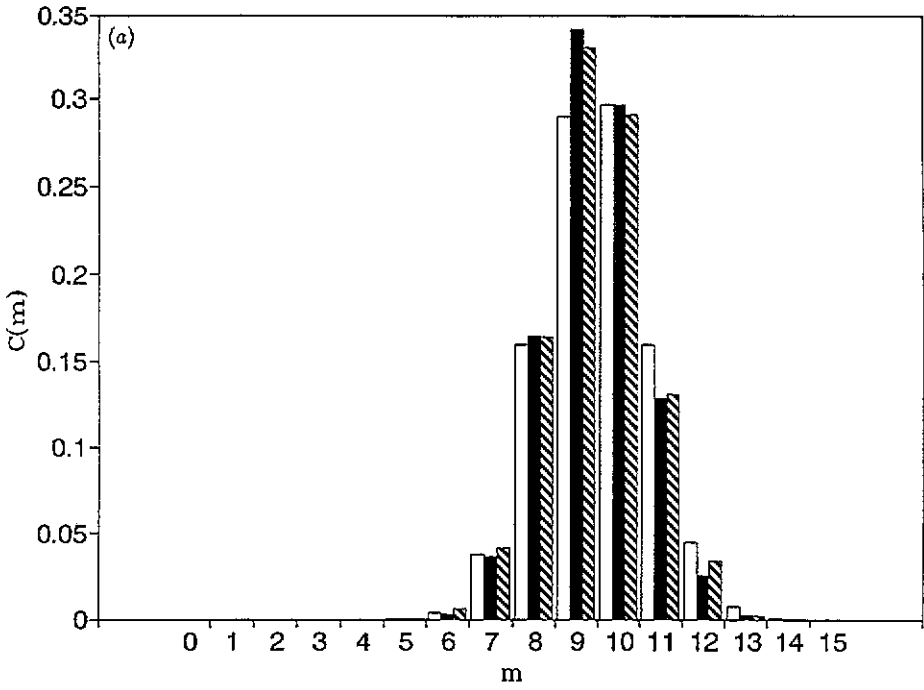
Figure 2. Partial pair correlation functions calculated from the particle coordinates. (a) $g_{NiNi}(r)$; (b) $g_{NiB}(r)$; (c) $g_{BB}(r)$. Full curve: run 1 ('unconstrained'); dotted curve: run 2 ('pairs'); broken curve: run 3 ('chains').

In order to achieve 'pairing' and 'chain formation' of boron atoms, constraints on B-B partial coordination were imposed. In the former case every boron atom was required to have exactly 1 neighbour within 2.4 Å. In the latter case half of the boron atoms were required to have exactly 2 neighbours within the same distance, and the other half should have no boron neighbours in this way. It has to be noted that the above constraint is necessary but not sufficient for forming real chains, as constraints neither on B-B-B bond angles nor on the length of the chains were imposed. Indeed, the resulting objects were rather more like clusters than well defined linear chains. The distance for the boundary of the first B-B coordination shell was taken 2.4 Å from the corresponding experimental study [8].

As a starting configuration both an FCC lattice with randomly distributed boron sites and a hard sphere (random) configuration were used. No alterations were observed in the final particle distributions as a result of different starts. For starting the 'constrained' calculations the final particle configuration of the 'unconstrained' simulation was used. Hereafter the 'unconstrained' calculation will be referred to as 'run 1', the constraint for pairing as 'run 2', and the constraint for forming chains as 'run 3':

Due to the extremely high number density some extra manipulations were needed during the simulations. In order to allow particles to change their local topology—and not to 'freeze' in their initial configurations—the hard sphere diameters of atoms have been lowered by 10–15 % several times, for periods of $2-5 \times 10^4$ accepted moves. For the same purpose, moves of 5–10 Å were forced and this resulted effectively in some particle switchings.

Figure 1 shows fits for run 1 after 1 million accepted moves. The curves for run 2 and run 3 are identical to those of run 1, therefore they are not shown separately. The overall



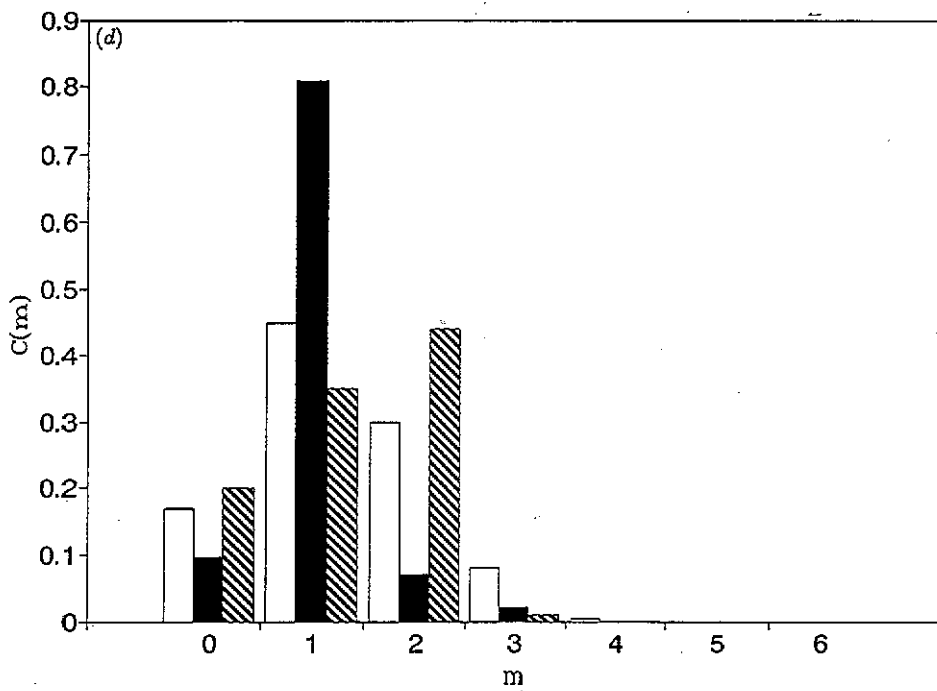
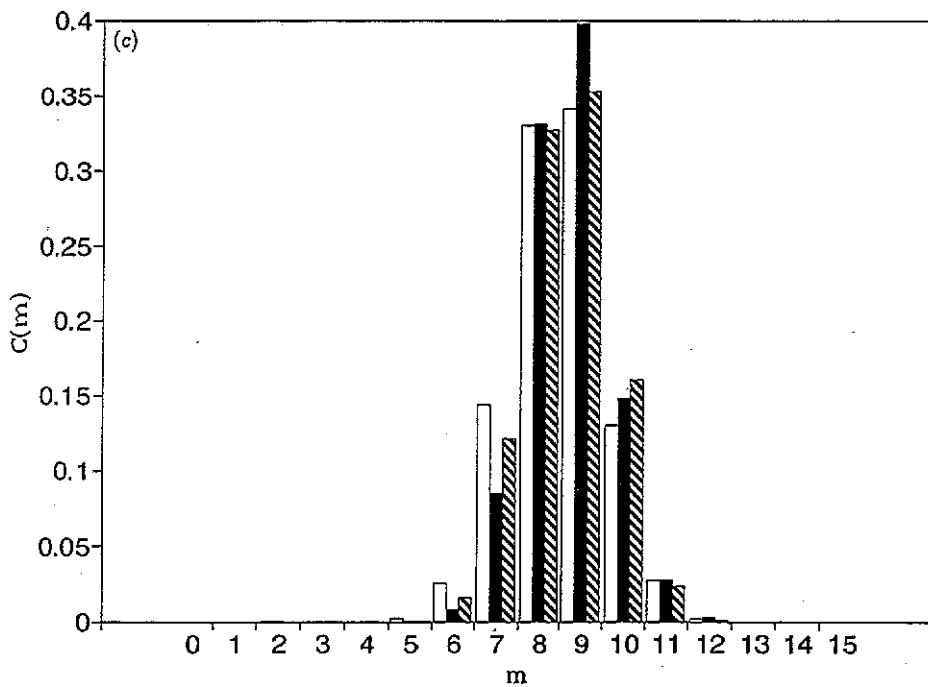


Figure 3. Distributions of the number of first neighbours, $C(m)$, for (a) B-B; (b) B-Ni; (c) Ni-B and (d) Ni-Ni pairs. Empty bars: run 1; filled bars: run 2; shaded bars: run 3.

agreement is acceptable, there is only one point that had to be inspected more closely. It is the disagreement between measured and model $F(Q)$ of figure 1(a) (natural abundance of Ni isotopes), and less seriously, $F(Q)$ of figure 1(b) (^{60}Ni isotope) in the range of 5–10 \AA^{-1} . It can be explained knowing that experimental values of $F(Q)$ were constructed from two parts: at relatively low Q , ($0.4 \text{\AA}^{-1} < Q < 10 \text{\AA}^{-1}$) they were measured at a steady state reactor while at higher Q values ($5 \text{\AA}^{-1} < Q < 30 \text{\AA}^{-1}$) at a pulsed neutron source. The interference falls exactly on the problematic regime between 5 and 10 \AA^{-1} . Looking at the original paper (see figure 1 of [8]) similar discrepancies can be seen between the two distinct parts as between RMC and the experiment. Also, if one transforms these $F(Q)$ s directly to total pair correlation functions, and, omitting the unphysical oscillations at low r , carries out the reverse transformation into Q space, then the resulting $F(Q)$ s are closer to the RMC solutions than to the original data. On this basis it can be stated that the RMC fits are within the limits allowed by the present experiment.

In order to investigate local orientational ordering some further definitions are needed. (Methods for characterizing the short-range structure are described by [6] in detail.) In this work the first coordination shells of particles were considered. The boundary of this shell was fixed at the position of the first minimum of the corresponding partial pair correlation function, $g_{\alpha\beta}(r)$. Atoms within this shell will be called 'neighbours', and vectors joining centres and neighbours are to be called 'bonds', implying no connection with any chemical bonding. Angles determined by two bonds will therefore be called 'bond angles'.

Possessing the Cartesian coordinates of every atom, it is possible to calculate the *distribution* of the number of neighbours in the first coordination shell, $C(m)$. $C(m)$ can also be considered as the distribution of the usual 'coordination number', therefore the importance of the average coordination number as a single quantity decreases. $C(m)$ can also give some idea of the extent of local ordering, through the width of the distribution.

The distribution of cosines of bond angles is a widely accepted means of characterizing local order [6]. $B_{\alpha\beta\gamma}(\cos \Theta)$ are defined as the number of bond angles with cosines falling between $\cos \Theta$ and $\cos \Theta + \Delta(\cos \Theta)$, divided (i.e. normalized) by the number of angles. For a two component system there are six such distributions, of which only the four most important are discussed here: $B_{\alpha\alpha\alpha}(\cos \Theta)$, $B_{\alpha\beta\alpha}(\cos \Theta)$, $B_{\beta\alpha\beta}(\cos \Theta)$ and $B_{\beta\beta\beta}(\cos \Theta)$.

3. Results and discussion

Comparing the curves of figure 1 to similar ones available in the literature for different structural models (see e.g. [3]) it is thought to be apparent that so far RMC has produced the model which possesses the highest level of consistency with experimental data, as far as the entire range of the experimental information is concerned. (See also [11].)

The three partial pair correlation functions calculated directly from particle positions are shown in figure 2 for each simulations. It is interesting to note that $g_{\text{NiNi}}(r)$ and $g_{\text{NiB}}(r)$ obtained from run 1 indicate slightly more ordered structure around the second (split) peak than those obtained from the 'constrained' calculations. $g_{\text{BB}}(r)$ is practically the same for all the three models. It seems like introducing constraints on the B–B distribution causes disordering on the *other* partial distributions.

Concerning the B–B contact found in experimental studies [8,9] its existence is confirmed by the present simulations. All the three structural models proved to be consistent with a peak of $g_{\text{BB}}(r)$ related to an average coordination number close to one, at around 1.9 \AA .

Figure 3(a) gives the distributions of the number of boron atoms in the first coordination shell of borons for all the three models investigated. Naturally, the average value is the

same as obtained from experiments; only the distributions alter significantly. The fraction of boron atoms with exactly 1 neighbour (in run 2) is around 80%, while that of boron atoms with exactly 2 neighbours (in run 3) is just above 40%. This means that the two structural models suggested [12] could not be fully realized in the present calculations. 'Pairing' of B atoms could be achieved more successfully than forming chains. In itself this does not automatically mean that formation of boron pairs is more likely than the formation of chains, since for the latter a more complex criterion has to be fulfilled. As the formation of *linear* chains was not carried out successfully (see section 2), and the original model would require a higher level of linearity, results from run 3 will not be considered rigorously. However, the values quoted above are significantly different from that of run 1, and therefore the distinction between the models is justified.

Average partial coordination numbers for the other types of atomic pairs also agree with those found in experimental studies [8, 9]. The constraints on the B-B distribution did not change their values, whereas the formation of B pairs causes slightly narrower distributions than found in run 1 and run 3 (see figures 3(b-d)). This is not reflected in other features (see figures 2 and 4), probably because Ni 'cages' formed around B *pairs* do not fit in the first coordination shell of a single B atom. It is interesting to note, however that the sharpening of the distribution corresponding to run 2, in comparison with those of run 1 and run 3, is the most apparent for $C_{BNi}(m)$ (see figure 3(b)).

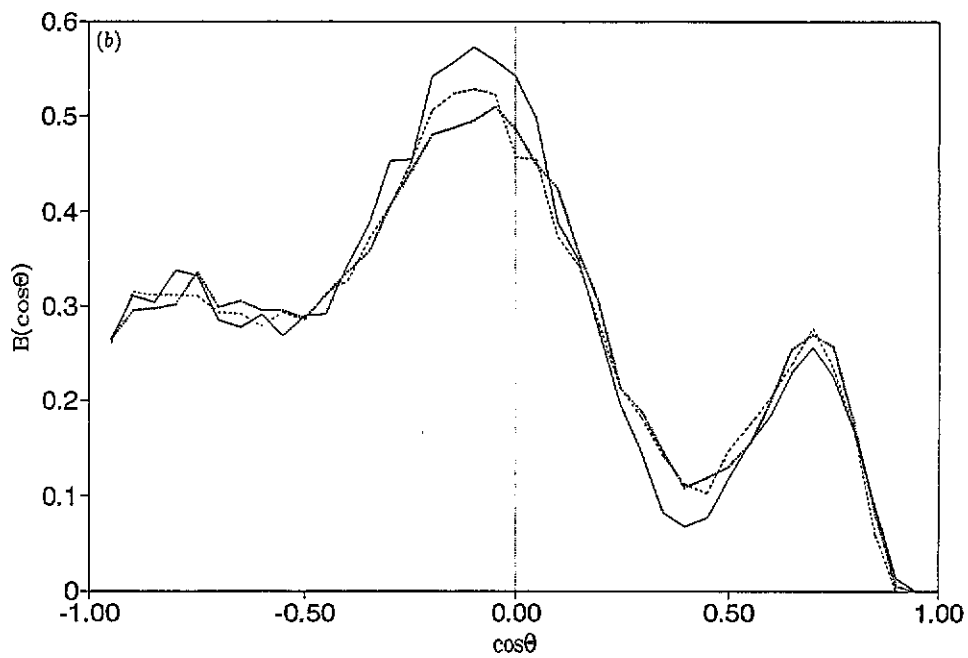
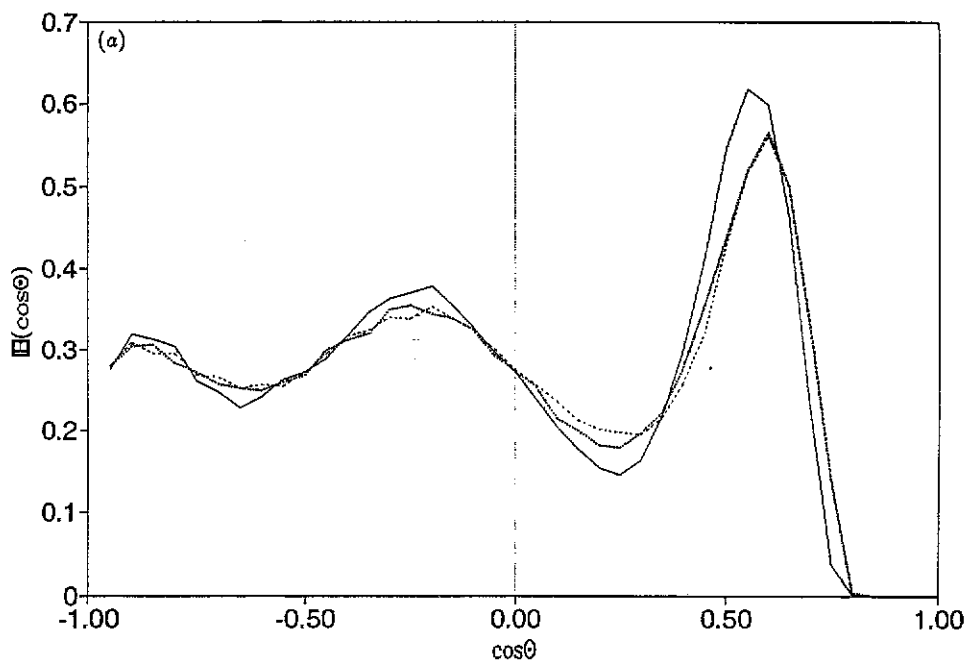
Figure 4 compares the four calculated $B_{\alpha\beta\gamma}(\cos \Theta)$ distributions for run 1, run 2 and run 3. The sharp details of these curves are remarkable, showing considerable short range ordering. In accordance with the corresponding values of $g_{\alpha\beta}(r)$, cosine distributions from run 1 imply slightly more pronounced local symmetries than those from run 2 and run 3. There are much smaller differences, however, between functions corresponding to run 2 and run 3.

It has already been found [9] that the present system exhibits considerable short-range ordering. The main manifestation of this is that the B-B first coordination number is *only* ≈ 1 , whereas it is ≈ 3 in a hard sphere (random) system of the same parameters. This short range order, which is the result of a sort of negative non-additivity of the atomic radii, is responsible for the rather strange shape of $B_{BBB}(\cos \Theta)$.

The fact that the peaks of these distributions are never found at regular angles like 60° , 90° or 180° , but they are always just nearby, like at 55° , 100° and 170° for $B_{NININi}(\cos \Theta)$, or at 35° , 95° and 170° for $B_{BNiB}(\cos \Theta)$, is noteworthy and not yet fully understood. On the grounds of $B_{NININi}(\cos \Theta)$ (and of $B_{NiBNi}(\cos \Theta)$) it seems that the metallic component forms a kind of 'substructure' whereas metalloids atoms can move more freely.

Comparing these distributions to cosine distributions of $Ni_{62}Nb_{38}$ [13] which is a different (metal-metal) type of metallic glass, three interesting observations can be made (figure 5). First, $B_{NININi}(\cos \Theta)$ of $Ni_{65}B_{35}$ resembles $B_{NININi}(\cos \Theta)$ and $B_{NbNbNb}(\cos \Theta)$ of $Ni_{62}Nb_{38}$, rather than the corresponding Ni-Ni-Ni distribution which peaks at 180° . Secondly, the shape of cosine distributions in $Ni_{62}Nb_{38}$ depends almost exclusively on the type of *central* atoms, but not on that of the neighbours. In $Ni_{65}B_{35}$ all the four distributions are distinctly different. Finally, cosine distributions of $Ni_{62}Nb_{38}$ suggest considerably better defined local symmetries than those of $Ni_{65}B_{35}$.

In agreement with previous studies [8] we have found that the inherent structure for this glass is *not necessarily* that of the corresponding crystalline counterpart, Ni_2B . However, cosine distributions of bond angles for $Ni_{65}B_{35}$ are very similar to those of $Ni_{81}B_{19}$ (see [11]), and therefore they can be originated to crystalline Ni_3B [11]. This finding supports the idea that the distorted crystalline Ni_3B structure can serve as a prototype Ni-B glassy structure [2].



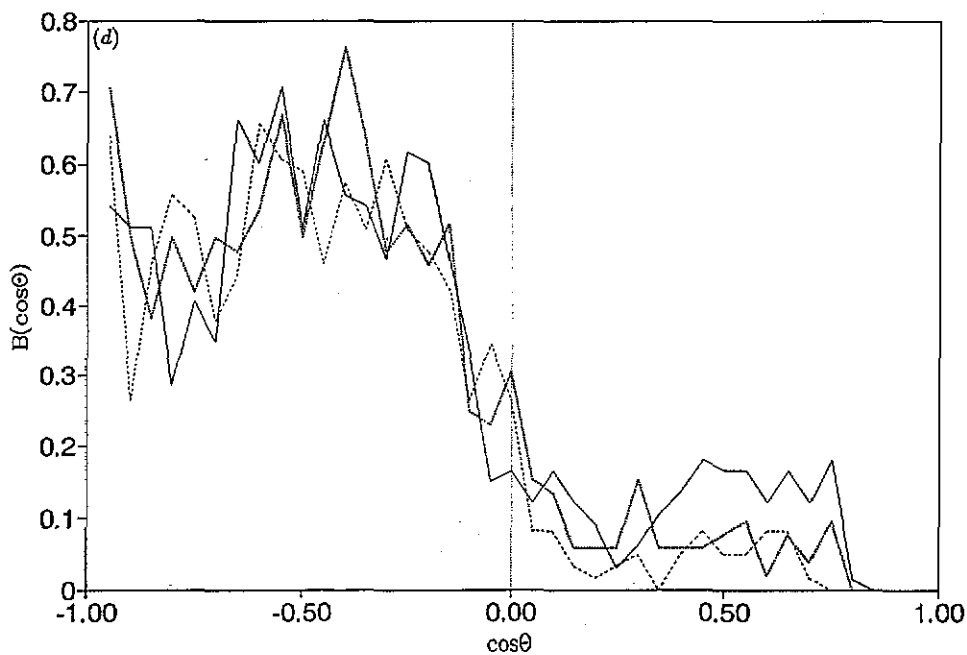
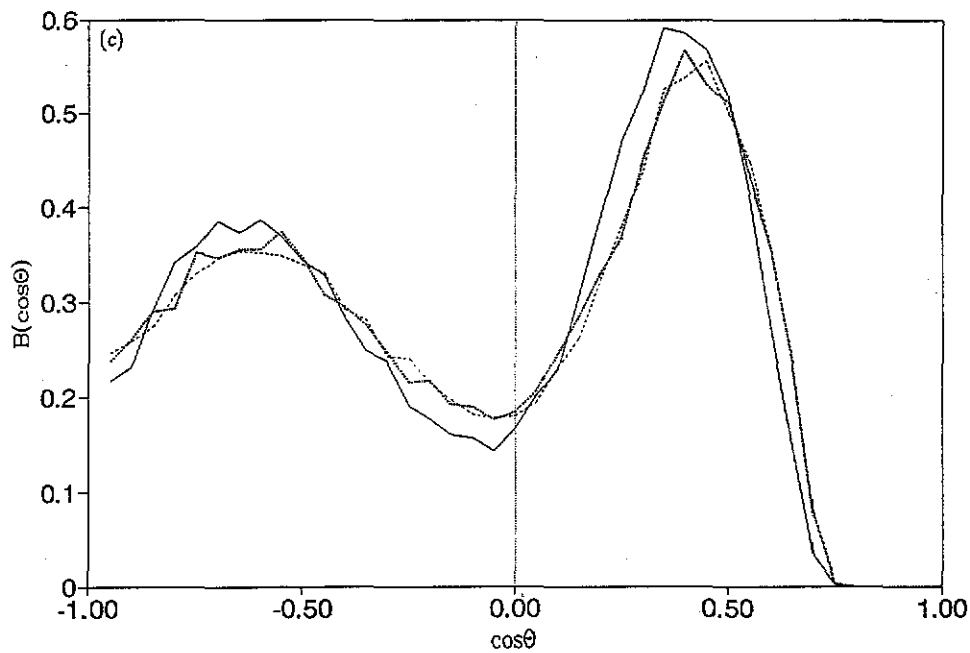
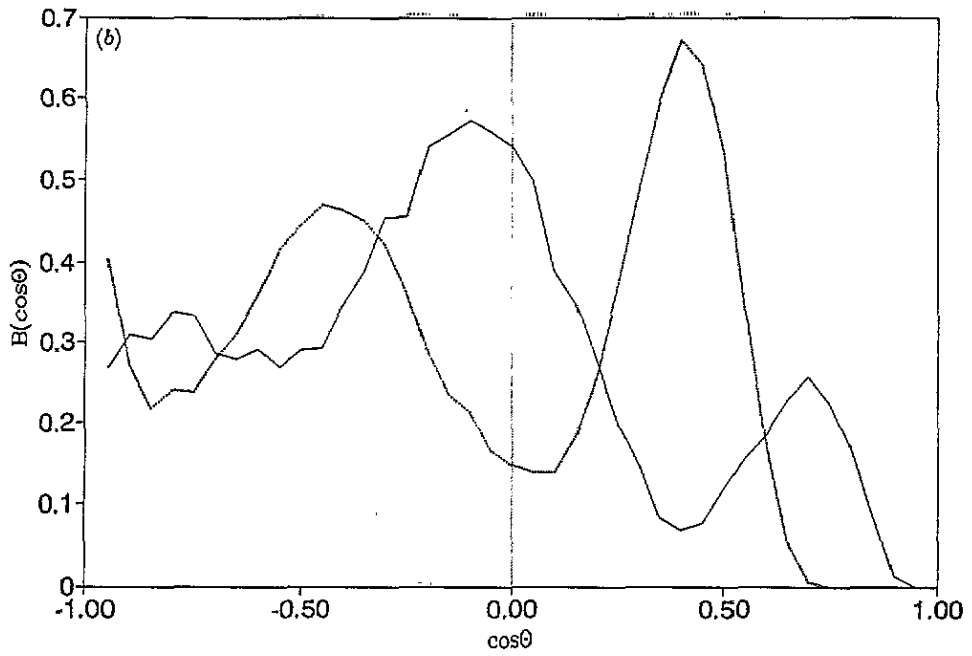
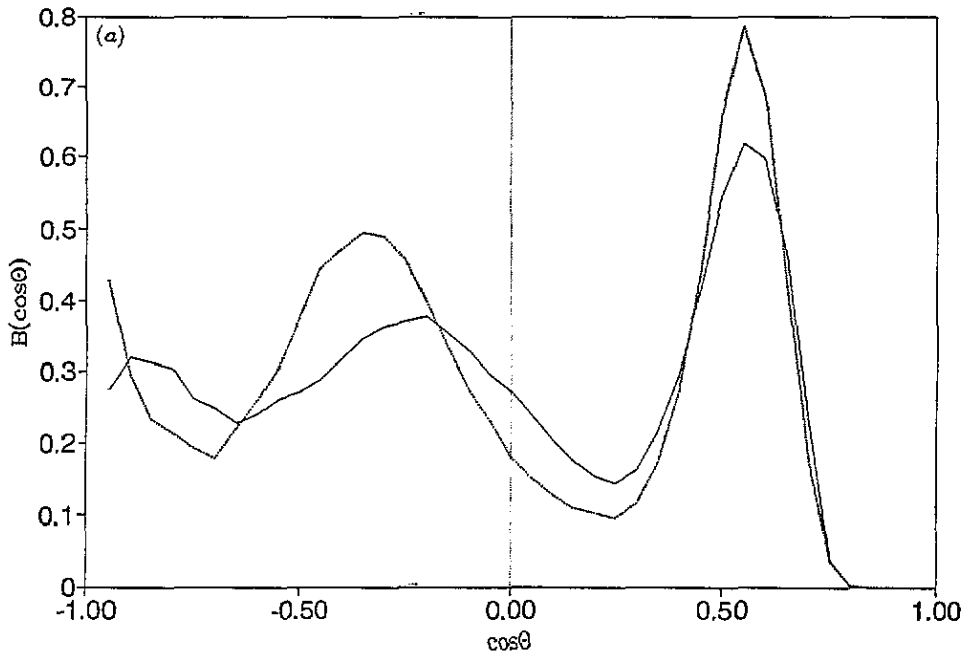


Figure 4. Cosine distribution of bond angles for amorphous $Ni_{65}B_{35}$. (a) $B_{NiNiNi}(\cos \Theta)$; (b) $B_{BBNiB}(\cos \Theta)$; (c) $B_{NiB}(\cos \Theta)$ $B_{BBB}(\cos \Theta)$. Full curve: run 1; dotted curve: run 2; broken curve: run 3.



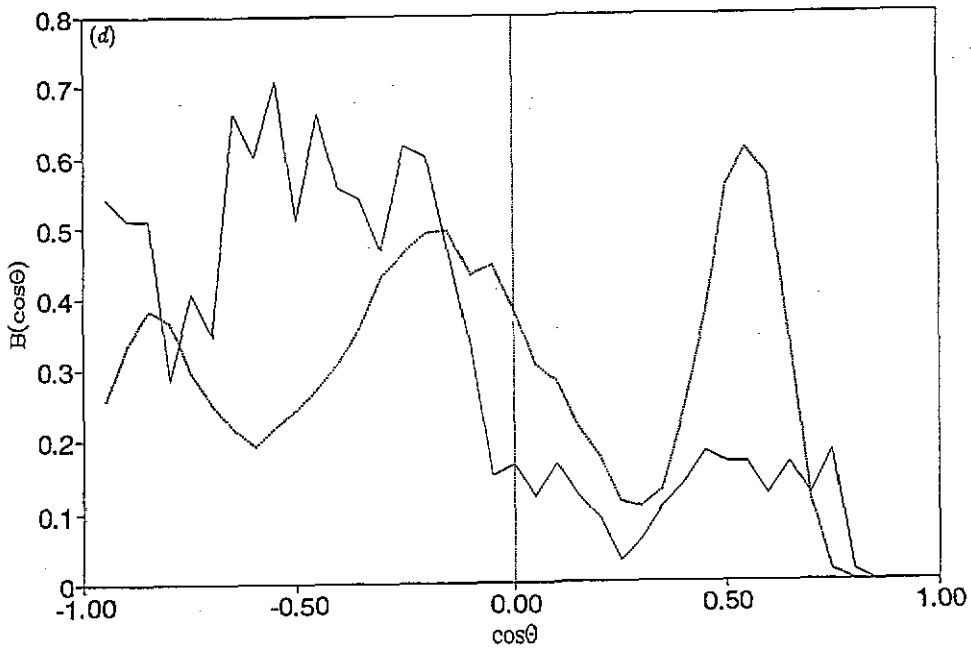
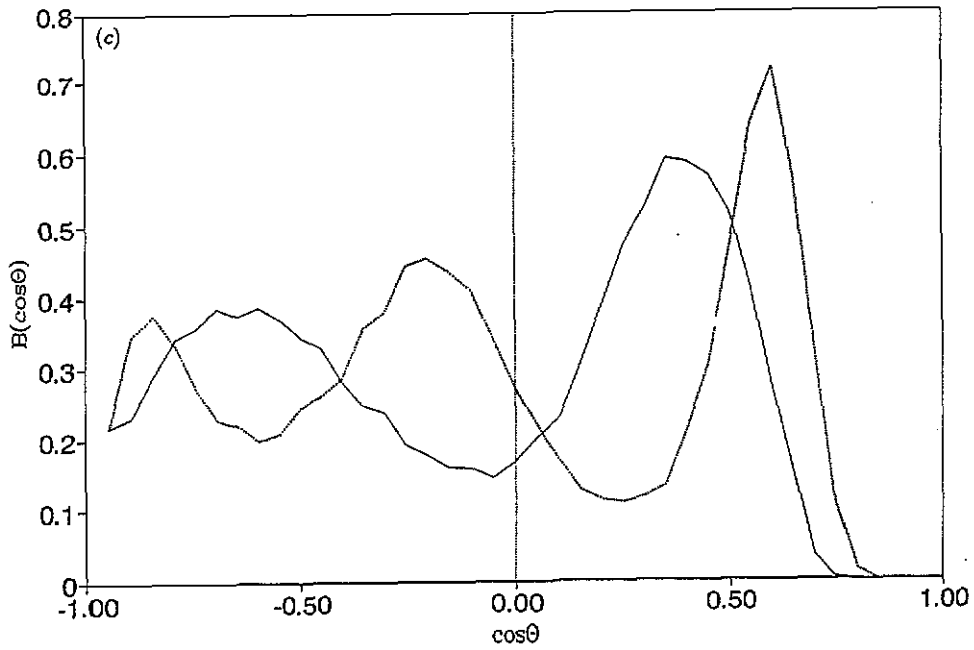


Figure 5. Comparison of cosine distribution of bond angles for amorphous $Ni_{65}B_{35}$ (run 1, 'unconstrained') and $Ni_{62}Nb_{38}$ (taken from [13]). (a) $B_{NiNiNi}(\cos \Theta)$; (b) $B_{XNiX}(\cos \Theta)$; (c) $B_{NiXNi}(\cos \Theta)$; (d) $B_{XXX}(\cos \Theta)$. Full curve: $Ni_{65}B_{35}$ ($X = B$); dotted curve: $Ni_{62}Nb_{38}$ ($X = Nb$). (Note that $B(\cos \Theta)$ intensities are *not* proportional to the number of angles.)

4. Conclusions

Reverse Monte Carlo modelling of the microscopic structure of metallic glassy $\text{Ni}_{65}\text{B}_{35}$ was carried out. Apart from the 'unconstrained' calculation the possibilities of 'pairing' and 'chain formation' of boron atoms were also investigated. Results from these three independent investigations do not differ significantly. This shows that on the basis of the present diffraction experiment it is not possible to distinguish the models proposed. In the 'unconstrained' configuration boron pairs and chains (clusters) coexist (also, with lone B atoms).

The main structural consequences are as follows:

(i) It is confirmed by the present study that a boron–boron contact at around 1.9–2.0 Å *does* exist, with an average of 1 B atom in the first coordination shells of B atoms, in accordance with previous findings [8,9].

(ii) On the grounds of neighbour distribution functions and cosine distribution of bond angles it is clearly shown that Ni–Ni and B–Ni local arrangements are highly ordered, whereas Ni–B, and mainly B–B arrangements are more disordered. This indicates that Ni atoms have a well defined, ordered arrangement while boron atoms seem to be scattered inside the nickel substructure rather randomly.

(iii) The features found for local symmetries do not imply close connections between glassy $\text{Ni}_{65}\text{B}_{35}$ and its crystalline counterpart, Ni_2B , but the close relations with $\text{Ni}_{81}\text{B}_{19}$ (and crystalline Ni_3B) are apparent. This is also in accordance with previous findings [8,11].

Acknowledgments

The authors are grateful to Dr R L McGreevy for the many helpful discussions. Thanks are due to Dr T Kemény and Dr I Vincze for their stimulating ideas. LP wishes to thank the Széchenyi István Scholarship Foundation for financial support during part of this work. He is also grateful for the help of the Alapítvány a Magyar Felsőoktatásért és Kutatásért Foundation. This work was also supported by OTKA grants Nos F 4320 and 2934.

References

- [1] Lamarter P, Sperl W, Steeb S and Bietry J 1982 *Z. Naturf.* **37a** 1223
- [2] Sietsma J and Thijsse B J 1988 *J. Non-Cryst. Sol.* **101** 135
- [3] Gardner P P and Cowlam N 1985 *J. Phys. F: Met. Phys.* **15** 2553
- [4] McGreevy R L and Pusztai L 1988 *Mol. Simul.* **1** 359
- [5] McGreevy R L, Howe M A, Keen D A and Clausen K 1990 *IOP Conf. Ser.* **107** 165
- [6] McGreevy R L and Pusztai L 1990 *Proc. R. Soc. A* **430** 241
- [7] Allen M P and Tildesley D J 1987 *Computer Simulation of Liquids* (Oxford: Clarendon)
- [8] Ishmaev S N, Isakov S L, Sadikov I P, Sváb E, Kőszegi L, Lovas A and Mészáros Gy 1987 *J. Non-Cryst. Sol.* **94** 11
- [9] Gardner P P, Cowlam N and Davies H A 1985 *J. Phys. F: Met. Phys.* **15** 769
- [10] Suzuki K, Fukunaga T, Itoh F and Watanabe N, 1985 *Proc. 4th Conf. Rapidly Quenched Metals* vol 1, ed S Steeb and H Warlimont (London: Elsevier) p 479
- [11] Iparraguirre E W, Sietsma J, Thijsse B J and Pusztai L, 1993 *Comp. Mater. Sci.* **1** 110
- [12] Kemény T and Vincze I 1992 private communication
- [13] Pusztai L and Sváb E 1993 *J. Non-Cryst. Sol.* **156-158** 973