Modelling of Partial and Total Radial Distribution Functions of Amorphous Ni_2B Using Reverse Monte Carlo Simulation

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Dedicated to Dr. Karl Heinzinger on the occasion of his 60th birthday

The use of Reverse Monte Carlo simulation, a novel method of structural modelling, looks very promising for the case of metallic glasses. In this paper initial results are shown for glassy Ni_2B, using experimental radial distribution functions as input information.

I. Introduction

The structures of metallic glasses have been studied for a long time by different diffraction techniques. For instance, several compositions of the typical metal-metalloid glass Ni_xB_{100-x} have been investigated by X-ray [1] and neutron [2, 3] diffraction methods. However, it was possible only in few cases to separate partial radial distribution functions, $g_{ij}(r)$, viz. only when isotopic substitution could be carried out [3]. There is only one structural feature, the coordination number, that can be calculated from $g_{ij}(r)$, but nothing about local symmetries can be said.

There is a novel method for structural modelling called Reverse Monte Carlo (RMC) simulation [4], which is able to provide deeper insight into the local structure. It is based on the results of diffraction experiments. A number of systems have so far been investigated by this method [5–9], and in all cases new structural information could be drawn from particle configurations which were present after RMC runs. Therefore it was quite straightforward to attempt to discover new features of the structures of metallic glasses by RMC. One might think that from the point of view of RMC these materials are similar to the formerly investigated ones, which were mostly molten and glassy ionic systems [5–7]. After a short trial period it turned out that some new problems had to be faced. It seemed therefore necessary to discuss the difficulties of modelling successfully the structures of such materials.

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II. Theory and Nomenclature

An exact definition of the functions obtained by diffraction measurements is essential for RMC. The data used in [3] were analysed according to the Aschroft-Langreth formalism [10] for binary mixtures, therefore it is shortly introduced here.

The partial radial distribution function, $g_{ij}(r)$, can be calculated from any simulation as

$$g_{ij}(r) = \frac{\varrho_{ij}(r)}{\varrho \cdot c_j}, \tag{1}$$

where $\varrho_{ij}(r)$ is the local number density of species j at distance r from the central particle of type i, ϱ the average number density and c_j the molar fraction of species j. The partial reduced radial distribution function, $G_{ij}(r)$, is

$$G_{ij}(r) = 4\pi\,\varrho\, r\,[g_{ij}(r) - 1]\,. \tag{2}$$

In Q-space the "Aschroft-Langreth partial structure factors (ALpsf)", $S_{ij}(Q)$, are applied, that can be obtained from $G_{ij}(r)$ as

$$S_{ij}(Q) = \sqrt{c_i\, c_j} \int_{r=0}^{r_{max}} G_{ij}(r) \sin(Q r)\, \mathrm{d}r\,, \tag{3}$$

which is expressed inversely by

$$G_{ij}(r) = \frac{2}{\pi \sqrt{c_i\, c_j}} \int_{Q=0}^{Q_{max}} Q\,[S_{ij}(Q) - 1] \sin(Q r)\, \mathrm{d}Q\,. \tag{4}$$

Relations between totals are somewhat different:

$$S(Q) = \int_{r=0}^{r_{max}} G(r) \sin(Q r)\, \mathrm{d}r \tag{5}$$

and

$$G(r) = \frac{2}{\pi} \int_{Q=0}^{Q_{max}} Q\,[S(Q) - 1] \sin(Q r)\, \mathrm{d}Q\,. \tag{6}$$

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$G(r)$ can be obtained from $G_{ij}(r)$ by

$$G(r) = \sum_i \sum_j \frac{c_i c_j \bar{b}_i \bar{b}_j G_{ij}(r)}{\sum_i c_i \bar{b}_i^2}, \tag{7}$$

while in Q-space

$$S(Q) = \sum_i \sum_j \frac{\sqrt{c_i c_j}\, \bar{b}_i \bar{b}_j S_{ij}(Q)}{\sum_i c_i \bar{b}_i^2}. \tag{8}$$

As it can be observed, in this formalism functions in r-space are normalized to zero, while those in Q-space are normalized to unity. Because of the non-uniformity of transformation of partials and totals the constants are not the same in r- and Q-space.

III. The Reverse Monte Carlo Procedure

The algorithm is very simple and can easily be understood by anybody familiar with "standard" (Metropolis) Monte Carlo technique (see e.g. [11]). A detailed description is given elsewhere [4, 7], thus only a brief summary is shown here.

(i) We start with an initial configuration which is a three dimensional array of N points in a cube of edge-length L. This configuration may be a lattice, may be generated at random or may be a result of an earlier simulation (MC, MD or RMC). Normal periodic boundary conditions [11] are applied, and then prdf's are calculated. From prdf's any $\mathbf{S}(X)$ structural function can be constructed which is relevant in a given diffraction experiment. (X can be r or Q, $\mathbf{S}$ can be g, G, or S.)

(ii) A new configuration is generated by a random motion of a randomly chosen particle (i.e. point) like in the normal MC, and the chosen $\mathbf{S}_{m+1}(X)$ is calculated for the $m+1$-th new configuration.

(iii) $\mathbf{S}_{m+1}(X)$ is then compared to experimental results, using a standard χ^2-test.

$$\chi^2_{m+1} = \sum_{i=1}^{n_x} (\mathbf{S}_E(X_i) - \mathbf{S}_{m+1}(X_i))^2 / \sigma_E^2, \tag{9}$$

where n_x is the number of X-points and σ_E is the experimental error assumed to follow a normal distribution at any X-point.

(iv) If $\chi^2_{m+1} < \chi^2_m$ the $m+1$-th configuration is accepted, otherwise it is accepted with a probability that follows a normal distribution with width σ_E. (This ensures the "simulation" of the experiment.)

(v) If the $m+1$-th configuration is accepted then it becomes the starting configuration, otherwise the m-th is retained. The process is then repeated from (ii).

After a certain, quite large number of accepted steps χ^2 decreases to an "equilibrium" value, about which it will then oscillate. At this point we can start collecting independent equilibrium configurations, and for them the calculated average $\mathbf{S}(X)$ will agree with experiment within the experimental error σ_E.

The computer time required for RMC is of the order of hours on a typical mainframe such as VAX 8800. No input potential is required, but experimental results of good quality are essential. There are two features of the set of prdf's obtained by RMC that cannot be achieved by any conventional data analysis:

- it is self consistent;
- it corresponds to real particle distributions, since prdf's were calculated from the particle configurations.

Owing to the presence of these particle configurations any structural information can be drawn from them, such as bond-angle distributions, bond orientational order parameters and many-body correlations.

IV. RMC for Amorphous Ni_2B

Partial and total reduced radial distribution functions of [3] were used as input for RMC simulation. Two different runs were performed: in Run 1 partial rrdf's, in Run 2 total rrdf's were modelled. In both cases 324 particles were put in a cubic box of side lengths $L = 14.72$ Å, which gave the experimental number density, $\varrho = 0.112$ Å^{-3}. One third of the points were identified as borons. For the purpose of an initial configuration a calcium-fluoride lattice was generated which seemed to be a convenient starting point. In both cases all the three partial radial distribution functions were calculated by (1).

In Run 1 three partial reduced rdf's were constructed according to (2). These calculated prrdf's were then compared with the experimentally obtained $G_{ij}(r)$. This comparison can be seen in Figure 1. The deviation between the two sets was 10% with the acceptance ratio of 1:12.

In Run 2 total reduced radial distribution functions were composed from the three $G_{ij}(r)$ on the basis of (7). Comparison between calculated and experimental trrdf's is shown in Figure 2. The deviation between the two (calculated and experimental) sets was found to be 15%. The ratio of accepted steps was 1:12.

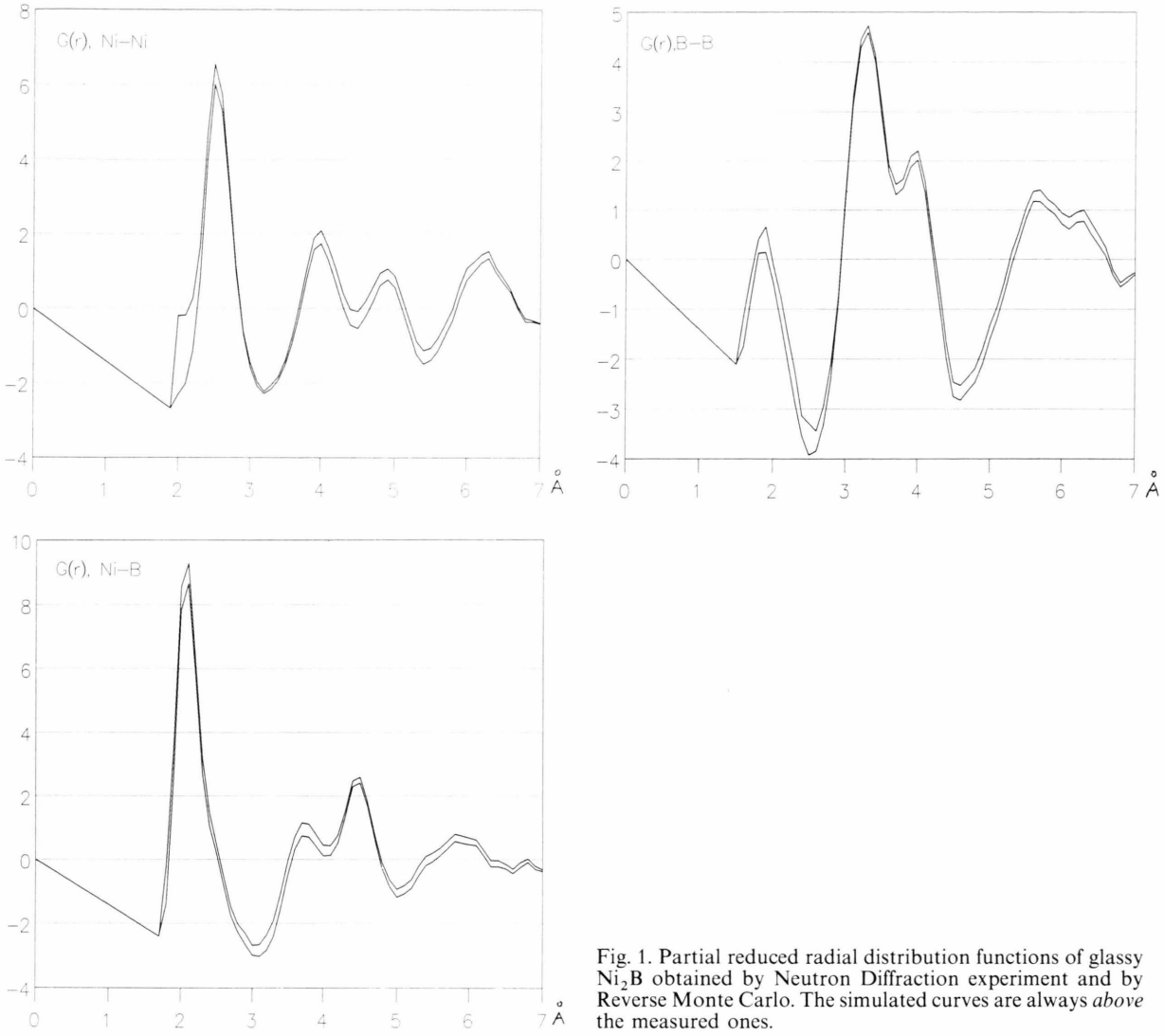

Fig. 1. Partial reduced radial distribution functions of glassy Ni_2B obtained by Neutron Diffraction experiment and by Reverse Monte Carlo. The simulated curves are always *above* the measured ones.

V. Discussion

Detailed structural analysis will be provided elsewhere [12]. There is one feature, however, which needs some more discussion, namely the relatively poor agreement between calculated and experimental radial distribution functions, comparing to the previously investigated cases [6]. It should be noted that there has never occurred such a problem in our practice before.

The most handy argument is the extremely high number density. It is much more difficult to find the equilibrium structure in a practically frozen system than in liquids. The role of the choice of the initial configuration must therefore be mentioned.

The structure of Ni_2B is very sharp at low r, and there are difficulties with the relatively coarse grid of r, where spacing is 0.1 Å. If one intends to lower this to its half, the number of particles should be increased in order to keep the quality of statistics.

The most proper way of analyzing a glassy structure would be the comparison at the structure factor level. For calculating $S(Q)$ from $g_{ij}(r)$ without large truncation errors the size of the simulated system should be greatly increased.

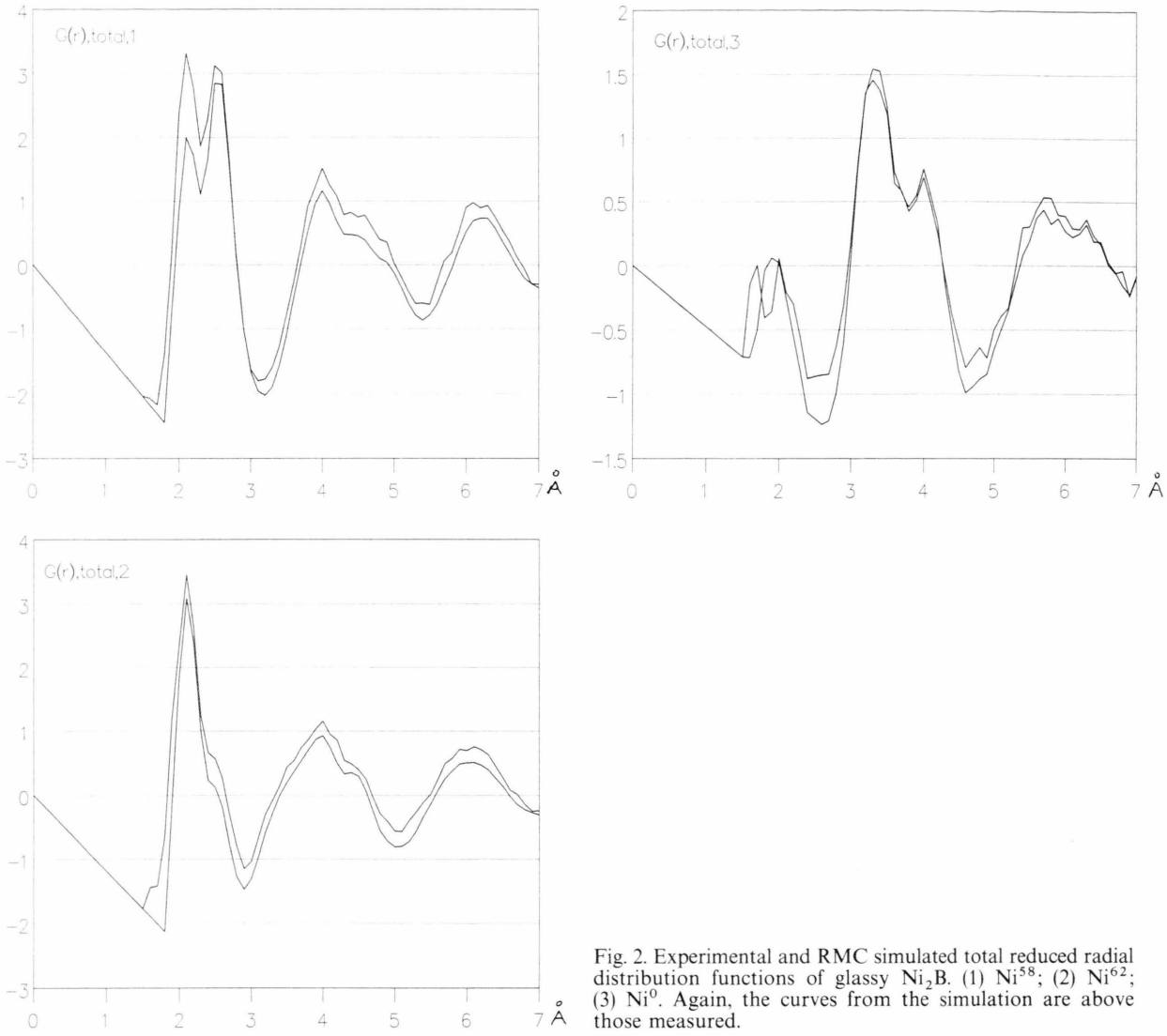

Fig. 2. Experimental and RMC simulated total reduced radial distribution functions of glassy Ni_2B. (1) Ni^{58}; (2) Ni^{62}; (3) Ni^0. Again, the curves from the simulation are above those measured.

VI. Conclusions

Further work is necessary for having fine details of the structure of metallic glasses. The new approach should include a proper choice of the initial configuration, and also larger systems should be used.

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