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# Computer simulation of medium-range order in amorphous transition-metal–metalloid alloys

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We present molecular-dynamics investigations of medium-range ordering in amorphous transition-metal–metalloid alloys based on interatomic forces derived from tight-binding-bond theory. We demonstrate that the small-angle scattering observed in Fe-rich $Fe_xB_{100-x}$ alloys ($x > 75$) arises from B-enriched regions of approximate composition $Fe_{75}B_{25}$ embedded in an Fe matrix. The formation of B-enriched regions is due to the strong covalent Fe-*d*–*B*-*p* bond.

The structural properties of metallic glasses are characterized by phenomena occurring on a wide range of length scales: The short-range order (SRO) is determined by the correlations of the atomic positions over a few nearest-neighbor distances; the medium-range order (MRO) depends on structural inhomogeneities with diameters ranging from ten to a few hundredths of Ångströms.[1,2] Scattering experiments have been instrumental in exploring both the short- and the medium-range order. However, as a diffraction experiment yields information only on a one-dimensional projection of the three-dimensional structure, other structure-sensitive probes and computer experiments are indispensable for the correct interpretation of the data.

The quality of a computer experiment depends on two essential features: the accuracy of the interatomic force field and the number of atoms in the microscopic ensemble used to describe a macroscopic material. A computer experiment is predictive only if the interatomic forces are derived from a sound quantum-mechanical description of the chemical bond, and predictions relating to the MRO order in particular are reliable only if the characteristic diameter of the model is distinctly larger than the range of the MRO phenomena.

In both respects, important progress has recently been achieved: we have developed a tight-binding-bond method for calculating interatomic forces in transition-metal and transition-metal–metalloid glasses and demonstrated its success in describing the chemical and topological SRO in these materials.[3-5] On the other hand, the advent of fast computers enables us to perform molecular-dynamics simulations of glass formation by rapid quenching from the melt on ensembles with 10 000 and more atoms. These models have diameters of up to $\simeq$ 50 Å, hence they can be used to describe MRO phenomena at length scales of $\simeq$ 20 Å. In the present report we describe molecular-dynamics investigations of MRO in $Fe_xB_{1-x}$ glasses supplementing our recent studies of SRO in a range of (Fe,Ni)–(B,P) glasses.[5]

Medium-range order in (Fe,Ni)–(B,P) glasses has been investigated using small-angle neutron and x-ray scattering,[2,6-10] high-resolution electron microscopy,[11] field-ion microscopy,[12] Mössbauer spectroscopy,[13] and Auger analysis.[14] The results show that structural inhomogeneities exist at two different length scales: (i) local defects with characteristic dimensions of 10–20 Å (depending on composition and the thermal history of the sample during and after the quench) and (ii) extended defects with dimensions of several hundred Ångströms. There is now a general agreement that the fluctuations at large scales are associated with magnetic defects such as domain walls. However, since such length scales are far beyond the scope of atomistic simulations, we shall not pursue this topic here. For the local defects, contrast variation by isotopic substitution in small-angle neutron-scattering experiments (SANS) has demonstrated that the local defects are associated with fluctuations in the concentrations rather than density fluctuations. Since the intensity of the SANS decreases on approaching the composition $T_{0.75}M_{0.25}$, it has been suggested that the concentration fluctuations in $T_xM_{1-x}$ glasses with $x > 0.75$ arise from incipient formation of boron-enriched regions of the stoichiometry $T_3M$ corresponding to the stable crystalline components in a boron-depleted matrix. This interpretation seems to be supported by field-ion microscopy[12] and by the fact that during crystallization of $T_xM_{1-x}$ glasses crystalline $T_3M$ compounds are formed.[15] However, so far no attempt to interpret the origin of the MRO has been made.

Our molecular-dynamics studies are based on the tight-binding-bond interatomic forces introduced in our previous paper (Ref. 5, hereafter referred to as I): within the local-density approximation for electronic exchange and correlation and a tight-binding description of the one-electron states, it can be shown that the total energy may be decomposed into a pairwise repulsive energy and a covalent bond energy,[16] $E_{cov}$. The bond energy is given by

$$E_{\rm cov} = \frac{1}{2N} \sum_{i,j}{}' \, t_{ij}\,(R_{ij})\,\Theta_{ij} \quad . \tag{1}$$

In Eq. (1) the sum is over all two-center bonds, $t_{ij}$ is the transfer integral, and $\Theta_{ij}$ is the bond order defined as the difference in the number of electrons in the bonding and antibonding states formed by the tight-binding orbitals on sites $i$ and $j$. For the $T$-$M$ glasses the dominant features of the bond arise from the strongly hybridized TB-band complex of $T$ $d$ and $M$ $p$ states. The

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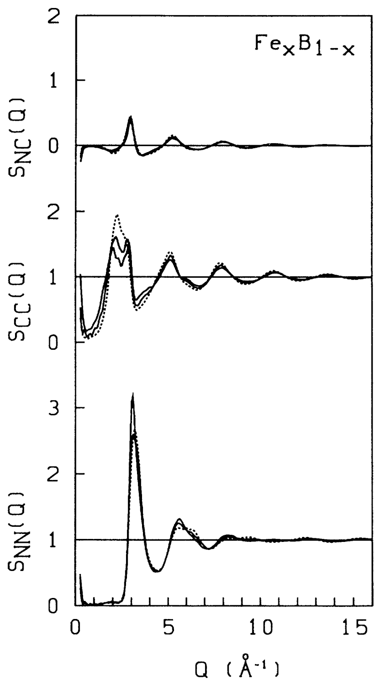

FIG. 1. Bhatia-Thornton partial structure factors $S_{NN}(Q), S_{NC}(Q)$, and $S_{CC}(Q)$ relating to number-density and concentration fluctuations in $\mathrm{Fe}_x\mathrm{B}_{100-x}$ glasses ( —, $x = 0.85$; - -, $x = 0.80$; $\cdots$, $x = 0.75$).

bond order $\Theta_{ij}$ depends on the atomic environment of the $i$-$j$ bond, hence Eq. (1) is the correct description of the many-atom forces. Two strategies for the calculation of the bond order have been proposed: (a) a decomposition of the bond energy in pair-, triplet-, and many-atom contributions via a moment expansion[17,18] of $\mathrm{E}_{\mathrm{cov}}$, and (b) a semianalytic calculation of $\Theta_{ij}$ on an appropriately chosen reference system, e.g., a Bethe lattice.[5] The moment expansion leads to a slowly convergent many-body series; the resulting many-body forces are too complex to be useful in large-scale computer simulations. The Bethe lattice approach models the local environment by only two parameters: the partial coordination numbers and bond lengths, but neglects the local topology of the lattice. This seems to be a legitimate approximation in a disordered system and allows for a summation contributions to infinite order by renormalized perturbation theory. The bond order is essentially proportional to the inverse square root of the coordination number $Z$, i.e., a summation over pairs of atoms leads to the characteristic square-root dependence of the total energy.[2,19] This shows that the physics behind the tight-binding-bond potentials calculated on a Bethe lattice is essentially equivalent to that expressed by the embedding potentials in

TABLE I. Interatomic distances $d_{ij}$ and partial coordination numbers $N_{ij}$ in amorphous $\mathrm{Fe}_x\mathrm{B}_{100-x}$ alloys (0.5 cm).

| | Fe-Fe | Fe-B | Fe-$X$ | B-Fe | B-B | B-$X$ |
|---|---|---|---|---|---|---|
| $\mathrm{Fe}_{85}\mathrm{B}_{15}$ | | | | | | |
| $N_{ij}$ | 11.72 | 1.71 | 13.43 | 9.71 | 0.02 | 9.73 |
| $d_{ij}$ (Å) | 2.50 | 2.18 | | 2.18 | 3.65 | |
| $\mathrm{Fe}_{80}\mathrm{B}_{20}$ | | | | | | |
| $N_{ij}$ | 11.19 | 2.40 | 13.59 | 9.61 | 0.09 | 9.70 |
| $d_{ij}$ (Å) | 2.51 | 2.27 | | 2.27 | 3.55 | |
| $\mathrm{Fe}_{75}\mathrm{B}_{25}$ | | | | | | |
| $N_{ij}$ | 10.64 | 3.16 | 13.80 | 9.47 | 0.22 | 9.69 |
| $d_{ij}$ (Å) | 2.50 | 2.20 | | 2.20 | 3.45 | |

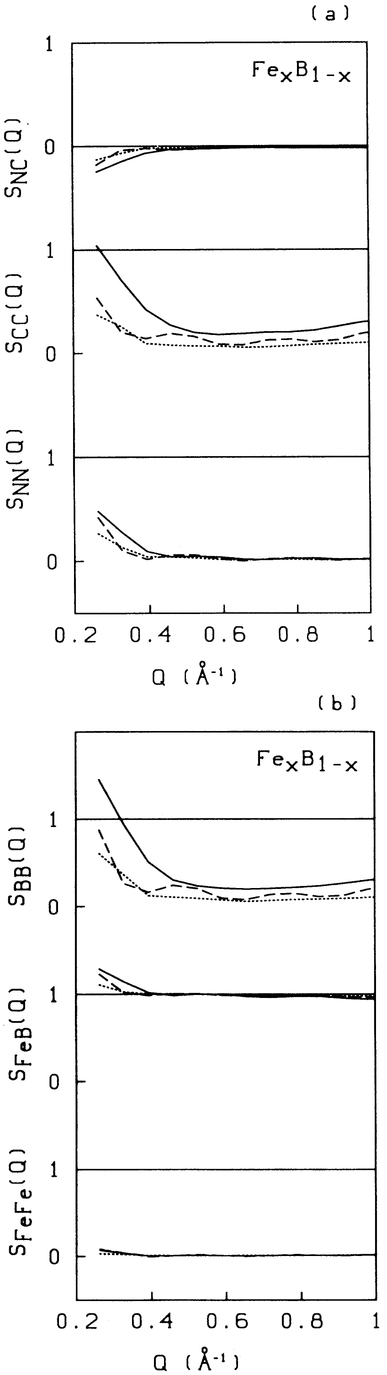

FIG. 2. (a) Bhatia-Thornton and (b) Ashcroft-Langreth partial structure factors of $\mathrm{Fe}_x\mathrm{B}_{100-x}$ glasses in the long-wavelength limit (—, $x = 0.85$; - -, $x = 0.80$; $\cdots$, $x = 0.75$).

a Finnis-Sinclair[20] or embedded-atom approach.[21] Formally, the covalent bond energy is reduced to pair forces, i.e., it assumes a form ideally suited for large-scale simulations.

The form of the pair interactions, however, is far from that of classical pair forces: the potentials are strongly nonadditive, with a distinct preference for strong and short $T$-$M$ bonds and $M$-$M$ interactions that are repulsive over nearest-neighbor distances. The potentials for $Fe_{80}B_{20}$ are given in Fig. 2 of I; they are only very weakly composition dependent for Fe contents varying between 90 and 75 at. % Fe.

The molecular-dynamics modeling of the quench and annealing procedure has been described in detail in I where the results for $N = 1372$ atom ensembles for $Fe_{80}B_{20}$, as well as for several amorphous Ni-B, Ni-P, and Fe-P alloys have been presented. Here we report simulations for $N = 10^4$ atom ensembles for $Fe_{85}B_{15}$, $Fe_{80}B_{20}$, and $Fe_{75}B_{25}$. Figure 1 shows the partial Bhatia-Thornton structure factors for the three alloys. We immediately notice the strong increase of the small-angle scattering with decreasing B content, but otherwise the partial structure factors indicate that the strong local chemical and topological order is hardly affected by the change in composition. This is also confirmed by the analysis of the nearest-neighbor distances and coordination numbers (Table I): all nearest-neighbor distances and the total coordination numbers of both the Fe and B atoms are essentially independent of compositions. The ratio of the total coordination numbers of Fe and B sites ($N_{\mathrm{Fe}} \simeq 13.5$ and $N_{\mathrm{B}} \simeq 9.5$, respectively) is determined by the repulsive diameters of the Fe-Fe and Fe-B interactions, together with a B-B potential supressing all direct B-B contacts. However, whereas at all concentrations each B atom is surrounded by about nine Fe atoms and no direct B-B neighbors, the distribution of Fe and B atoms around Fe sites changes essentially as expected in a chemically random alloy. This shows that the local order in the Fe-B

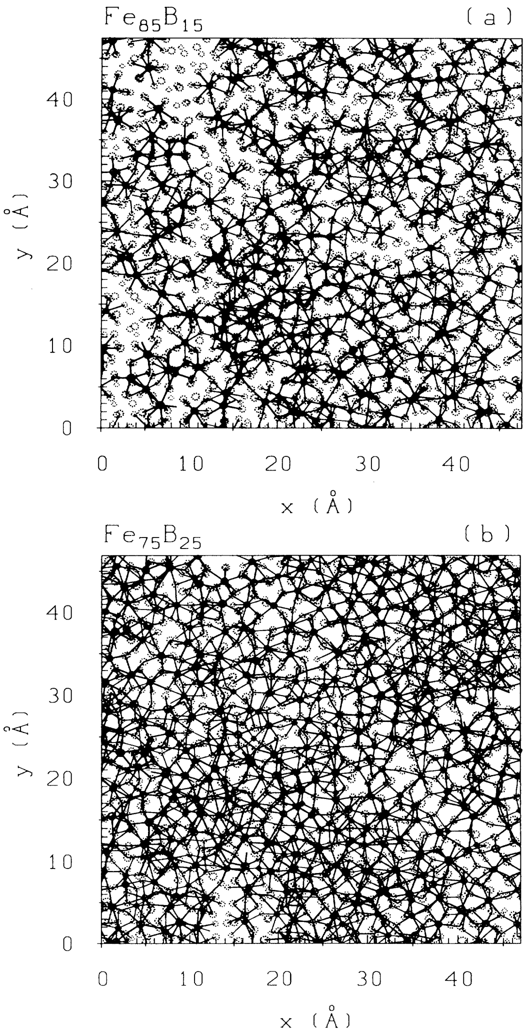

FIG. 3. Projection of layers of ~ 7 Å thickness cut out of 10 000-atom models of amorphous $Fe_{85}B_{15}$ (a) and $Fe_{75}B_{25}$ (b). Fe atoms are represented by broken circles, B atoms by full circles. Nearest-neighbor Fe-B bonds are drawn. See text.

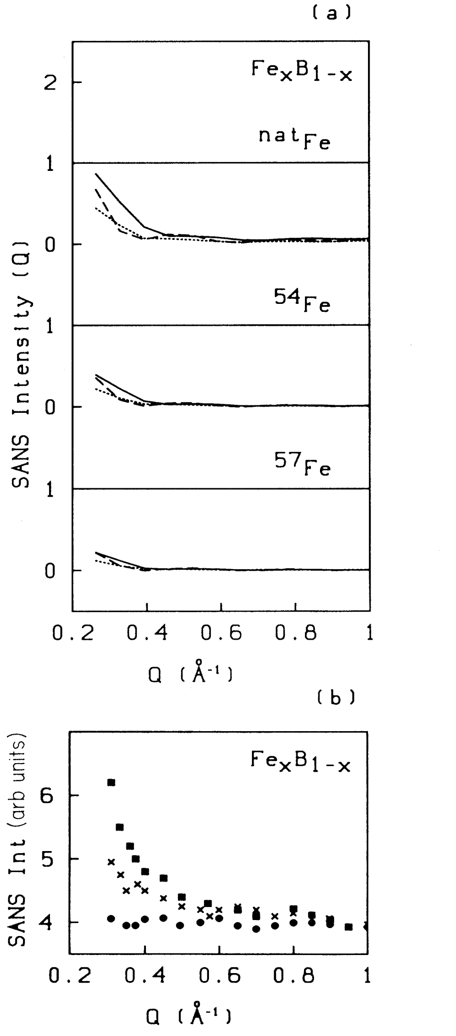

FIG. 4. (a) Intensity of small-angle neutron scattering (SANS) for amorphous $Fe_xB_{100-x}$ alloys (—, $x = 0.85$; - -, $x = 0.80$; ···, $x = 0.75$), calculated for various Fe isotope mixtures. (b) Experimental SANS intensities after Faigel and Svab (Ref. 8).

glasses is dominated by the strong covalent Fe-B bond. A coordination of the B atoms by nine Fe atoms, independent of composition, corresponds to the stereochemically defined models proposed by Gaskell[22] assuming that the metalloid sites are surrounded by nine metal atoms in the form of a caped trigonal prism. This is the local unit characteristic of the crystalline $T$-$M$ compounds. In I we have shown that the distribution of the bond angles around the $M$ sites is in agreement with a local trigonal prismatic order.

The medium-range order is also dominated by the strong Fe-B bond. Figure 2 shows the small-angle part of the partial structure factors. In the Bhatia-Thornton structure factors, the small-angle intensity is dominated by the concentration fluctuations, with a small contribution from density fluctuations. The component-related partial structure factors $S_{ij}(Q)$ [Fig. 2(b)] however show that the low-wavelength fluctuations arise from B-B correlations only, and that they strongly decrease on approaching the composition of the intermetallic compound $Fe_3B$. Lamparter and Steeb[2] have speculated that the small-angle scattering arises from regions of stoichiometry $Fe_{75}B_{25}$, embedded in an Fe-rich matrix. Whereas it is difficult to provide convincing evidence on the basis of scattering experiments alone, the computer experiment allows for a direct inspection of the local atomic geometry. Figure 3 shows the projection of slices (about 7 Å thick) of the 10 000-atom models of $Fe_{85}B_{15}$ and $Fe_{75}B_{25}$. The full lines show the B atoms and the network of Fe-B nearest-neighbor bands, the dotted circles represent the Fe atoms. It is immediately evident that $Fe_{85}B_{15}$ consists of B-rich regions with a dense network of B-Fe bonds, separated by thin layers containing almost no B. In $Fe_{75}B_{25}$, on the other hand, the Fe-B network is almost homogeneous. For $x > 0.75$, a Guinier fit of the small-angle scattering in the region $0.2\ \text{Å}^{-1} \leq Q \leq 0.6\ \text{Å}^{-1}$ leads to a radius of gyration of $R_G \sim (5 \pm 1)$ Å, corresponding to scattering regions of average diameter $D \sim (13 \pm 2.5)$ Å (assuming spherical scattering units). This is in good agreement with the experimental estimates.[2,9] A quantitative comparison must be based on the weighted average (concentrations, scattering lengths) of the partial structure factors. Figure 4 shows the SANS intensity, compared with the experimental data of Ref. 8. We note that although the SANS intensity decreases on approaching the "stoichiometric" composition $Fe_3B$, it does not completely disappear as suggested by the experimental data. We think that this is related to our simplified description of the covalent $p$-$d$ bond: a directional covalent bond saturates at the correct stoichiometry, because all bonding orbitals are occupied. The directionality of the bonds is neglected in our calculation of the bond orders on a Bethe reference lattice, leading a slight overestimate of the bond order. A more accurate treatment must consider the interrelation between the actual topology and chemical order of the amorphous network and the local bonding properties.

In summary, we have demonstrated that the combination of tight-binding-bond forces and of the possibility to perform molecular-dynamics simulations of the quenching process for large ensemble allows for the investigation of medium-range order in amorphous transition-metal-metalloid alloys at a level of detail not previously possible.

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