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Short-range order in Fe-B metallic glass alloys

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Measured hyperfine fields at iron sites in Fe-B glass alloys are compared to calculations based on two models. The first model is based on the concept of dense random packing of spheres; the second emphasizes the short-range order found in crystalline materials with similar compositions. The crystalline short-range order is found to give a better fit and suggests specific improvements in the concepts used to understand the atomic structure of glasses.

Experimental information on the atomic structure of metallic glass alloys has been obtained primarily from x-ray and neutron scattering. The full information content of these measurements can only be extracted by complex procedures. Even if all the individual pair distribution functions are determined separately, only the *average* atomic distances and coordination numbers can be obtained; no detailed information on the probability distributions of different possible atomic configurations is available. Attempts to bridge the gap between measured averages and actual order on a short-range scale involve the use of theoretical modeling.[1] It is important, therefore, to study physical properties which are sensitive to a local configuration.

In this paper, we will investigate how the chemical short-range order in ferromagnetic $Fe_{1-x}B_x$ glass alloys is reflected via the iron hyperfine field distribution, average magnetization, and hyperfine field. These quantities will be calculated on the basis of different models and compared with measured values taken from the literature.

The first model[1] consists of a dense, random packing (DRP) of spheres with different diameters; the chemical short-range order results from an energetic relaxation procedure (using Lennard-Jones pairwise interaction potentials) which is designed to forbid boron-boron nearest neighbors. The Fe-B interactions are strong in these models and have been shown[2] to favor the short-range order found at metalloid sites in crystalline cementite structured systems. A second calculation is based upon a model[3] assuming that strong Fe_3B-type short-range order exists at iron sites in these alloys.

It is well known from comparisons among various intermetallic compounds that both the hyperfine field at a given site and its magnetic moment are determined mainly by the number of nearest metalloid neighbors. For example, there is now significant evidence[4] that metastable Fe_3B is isostructural to the tetragonal Fe_3P intermetallic compound.[5] The structure has three crystallographically inequivalent iron sites $Fe_{(2)}$, $Fe_{(3)}$, and $Fe_{(4)}$ (in equal number), the nearest boron neighbors of which number $n_B = 2$, 3, and 4, respectively. The iron coordination shell is centered on 2.6 Å and contains two, ten, and ten atoms, respectively. The hyperfine fields of these iron sites,[3] $H_{Fe}(n_B)$, are shown in Fig. 1(a); also shown are the hyperfine fields measured on Fe_2B and FeB intermetallic compounds. Fe_2B iron sites have 4 B and 11 Fe nearest neighbors; FeB iron sites have 6 B and 10 Fe nearest neighbors.[6] All of these iron sites have nearly the same iron neighborhood, numbers varying only from 10 to 12; however, their boron environment varies widely and correlates with the variation observed in hyperfine field. The Fe hyperfine fields with 4 B neighbors taken from Fe_2B and Fe_3B (Fe^4 sites) agree to within 10%, showing that the dominant effect is determined by the number of boron neighbors; the small deviation is due to the different crystal structures. In the following calculation for the dependence of the iron hyperfine field on the number of boron neighbors we will use the values given in Fig. 1(a); the values for $n_B = 1$ and 5 are interpolated (since no intermetallic compound with such local environment exists), and for $n_B = 4$ the value measured on crystalline Fe_3B will be used.

Figure 1(b) exhibits the dependence of the iron magnetic moment, μ_{Fe}, on n_B, number of neighboring boron atoms. Measured values[7] are shown for

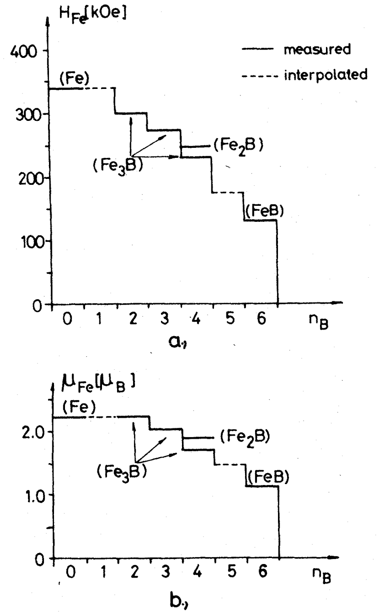

FIG. 1. Iron hyperfine fields (a) and magnetic moments (b) as a function of the number of nearest boron neighbors. Data are taken from Refs. 3, 6, 7, and 11. The values of the magnetic moments from Fe_3B were obtained using the proportionality between the magnetic moment and hyperfine field.

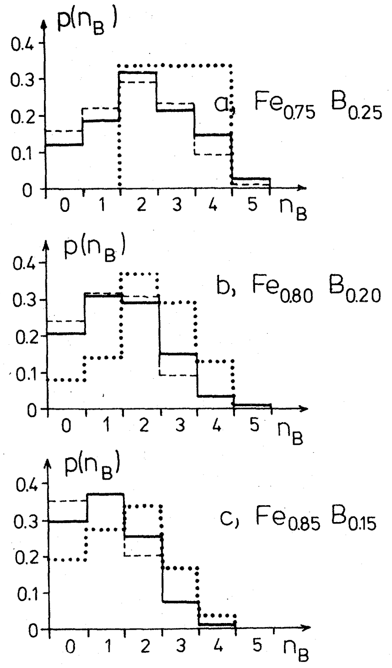

FIG. 2. Probability distribution of the iron atoms with different number of boron neighbors calculated in a DRP model with different boron concentration. The full line was used in our further calculations. Full line $r \leq 1.1 (r_{Fe}+r_B)$, dashed line $r \leq 1.05 \times (r_{Fe}+r_B)$. Dotted lines are $p(n\ )$ for the quasicrystalline model.

Fe_2B and FeB; however, for Fe_3B, the well-established proportionality[5,8] between the hyperfine field and magnetic moment was used to deduce μ_{Fe} as a function of n_B from the measured iron hyperfine fields (direct neutron measurements have not yet been made).

Our first calculation is based on the probability distribution of iron atoms with different numbers of boron neighbors, $p(n_B)$, determined from DRP models. Three models were studied whose average properties have previously been published[1]: $Fe_{75}B_{25}$, $Fe_{80}B_{20}$, and $Fe_{85}B_{15}$. The first has the same composition as the stoichiometric intermetallic compound Fe_3B, the second is near the center of the composition range over which glass formation is possible, and the third is near the end of that range. Each nonsurface iron site in each model was examined for neighbors within a fixed distance; iron and boron neighbors were tabulated separately[2]. Figure 2 displays $p(n_B)$ determined from these tabulations. There is a problem in deciding which atoms to count as near neighbors and which to exclude. In the statistical average studies,[1] one usually assumes that near neighbors are those atoms which lie within the distance corresponding to the first minimum in the appropriate partial pair distribution function; for the present work we found this to be highly unsatisfactory. We began with the hard-sphere touching distance, defined by the minima in the relaxation potentials, and added (5, 6, ..., 10, ..., 12, 13)% of that distance. The calculated distributions, $p(n_B)$, changed considerably from 5% to 10% but very little beyond that; the distributions for both 5% and 10% are shown in Fig. 2. Pragmatically, we use $1.10(r_{Fe}+r_B)$ as the distance within which to count boron neighbors.

The important feature to note in Fig. 2 is the broadening of $p(n_B)$ with increasing boron concentration (in analogy to the behavior of disordered alloys). Having $p(n_B)$ and the numbers measured or deduced for $H_{Fe}(n_B)$ and $\mu_{Fe}(n_B)$ we can calculate the average values $\overline{H}_{Fe}$ and $\overline{\mu}_{Fe}$ as a function of boron concentration x. The full lines show the results in Figs. 3(a) and 3(b); in both cases the calculated values are well above the measured values. Also shown in Fig. 3(b), for reference, is $\overline{\mu}_{Fe}(x)$ calculated on the basis of a donor model fitted to μ_{Fe_2B} and μ_{FeB} which corresponds to 1.6 electrons transferred from boron to iron atoms. Clearly, this calculation gives a poorer estimate of $\overline{\mu}_{Fe}(x)$ than the DRP calculation because the donor concept used here is too crude.[9]

The probabilities of the configurations with $n_B = 0$, 1, and 2 seem to be overestimated by this model. Figure 4 shows this more clearly where the measured iron hyperfine field distributions are compared to those calculated on the basis of the DPR model. The experimental distributions are shown as dashed histograms. The vertical lines are located at the hyperfine fields for sites with different numbers of boron neighbors [given in Fig. 1(a)] and their heights are proportional to the probabilities $p(n_B)$ for a specific model (given in Fig. 2); each contribution is broadened by a Gaussian distribution whose width ΔH is taken to be proportional to the value of the hyperfine field H as previously described[3] (specifically $\Delta H/H = 0.103$, as deduced below). The $p(H)$ curves calculated in this manner show the characteristic narrowing (present in a random model) for decreasing x. In all cases the high field probabilities (i.e., low boron coordinations) are substantially overestimated. The apparent overabundance of low boron coordinated iron sites is most likely connected with the relaxation potentials used. The Fe-B interaction was taken to be twice as strong as that between Fe sites; thus the relaxation concentrated on producing B sites with highly specific coordinations[2] which have been described[1] as packed molecular units. The iron atoms "squeezed out" of these units are too frequently coordinated by a shell of nearly all iron sites. Alternately, an increase in the "size" of the boron atom used in the modeling would shift the distributions in the right direction by having near neighbor shells large enough to contain more iron atoms. This structural refinement will be the subject of further work.

The $Fe_{75}B_{25}$ glass is exceptional in the sense that at crystallization it transforms[10] into a single metastable Fe_3B phase; it is, therefore, important to investigate the nature of the short-range order of a glass at this composition. It has been shown[3] that the $p(H)$ of this glass can be well described with the assumption that its local environments are similar to those in the Fe_3B compound. The calculated $p(H)$ is reproduced in Fig. 5(a); the only parameter used in the fit is the value of $\Delta H/H = 0.103$. The similarity of short-range order is also reflected in the same values of average hyperfine field and magnetization for the glass and for the compound. The concept is further supported by the fact that the Co_3B intermetallic compound and the glass with the same composition have the same average magnetization.[12]

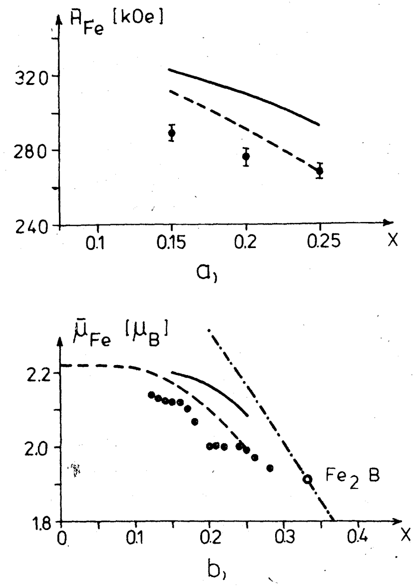

FIG. 3. Measured and calculated iron average hyperfine fields (a) and average magnetic moments (b) as a function of boron concentration. The hyperfine field data are taken from Ref. 10 and the magnetization data of Hasegawa and Ray (Ref. 14) were used. The full line is the calculated concentration dependence in a DRP model, the dashed line corresponds to the calculation in the quasicrystalline model with the assumption of random substitution of B by Fe. The dot-dash line show the calculated magnetization in the donor model as explained in the text.

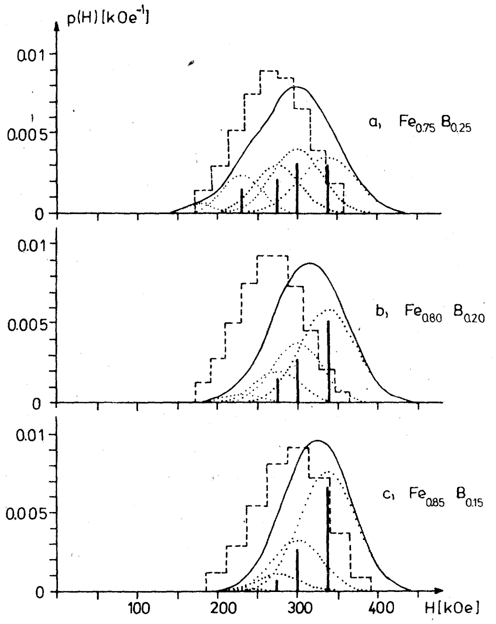

FIG. 4. Measured (Ref. 3; $T = 80$ K) and calculated (on the basis of a DRP model) iron hyperfine field distributions as a function of boron concentration.

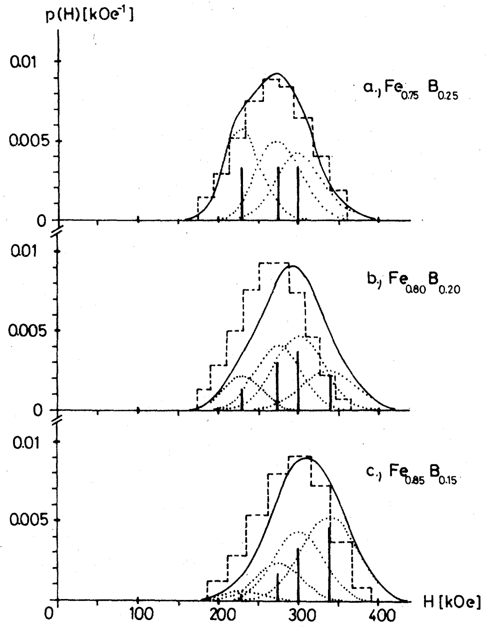

FIG. 5. Measured (Ref. 3; $T = 80$ K) and calculated (on the basis of randomly substituted quasicrystalline model) iron hyperfine field distributions as a function of boron concentration.

Our second model is based on the assumption that the short-range order in the glass is identical to that in the compound; deviation from the composition $Fe_{75}B_{25}$ is described by preferential substitution of Fe into the B sites. That is, we are describing the behavior of a nonstoichiometric compound, instead of the usual notation: $Fe_{1-x}B_x$, we should write $Fe_{0.75+y}B_{0.25-y}$, where y is the concentration of excess iron atoms. In effect, we are assuming a $p(n_B)$ as shown by dotted lines in Fig. 2(a).

If the substitution of B by Fe is random, we can calculate the probability of different configurations. If Fe_3B has the nickel phosphide structure[13] (as Fe_3P), all B atoms are crystallographically equivalent and have nine Fe nearest neighbors: four with 4 B ($Fe_{(4)}$), three with 3 B ($Fe_{(3)}$), and two with 2 B ($Fe_{(2)}$) neighbors. The probability that an iron atom having originally Z boron neighbors has K boron neighbors left after the substitution is given by a binomial distribution:

$$p(\mathrm{Fe}_K^Z)=\binom{Z}{K}(1-C)^K C^{Z-K}, \quad \begin{matrix} Z=2,3,4 \\ K=0,1,\ldots,z \end{matrix} ,$$

where $C=4y$ is the probability of the substitution of a given boron by iron. The relative number of iron atoms with K boron neighbors is

$$p(n_B=K)=\frac{0.25}{0.75+y}\sum_{Z} p(\mathrm{Fe}_K^Z)$$

$$=\frac{1}{3+C}\sum_{Z}\binom{Z}{K}(1-C)^K C^{Z-K}.$$

Combining these probabilities with the $H_{Fe}(n_B)$ and $\mu_{Fe}(n_B)$ values given in Figs. 1(a) and 1(b), we can calculate the concentration dependences of $\overline{H}_{Fe}$ and $\overline{\mu}_{Fe}$. The results are shown in Figs. 3(a) and 3(b). The calculated values of both $\overline{H}_{Fe}$ and $\overline{\mu}_{Fe}$ are increasing faster with decreasing x than the experimental values; however, the discrepancy is less than for the DRP model calculation. The $p(H)$ curves calculated in this random-substituted quasicrystalline model are compared with the measured ones. The description of $p(H)$ is also somewhat better in this model, but it can be seen that the decrease in the number of Fe atoms with 4 B neighbors is highly overemphasized in this calculation (low field side). This is the reason for the stronger than observed concentration dependence of the calculated $\overline{H}_{Fe}$ and $\overline{\mu}_{Fe}$.

The overestimation is due to the assumption of *random* substitution of boron by iron. The deviations can be explained if it is assumed that the substitutions are *correlated* in the following sense: after the first B has been replaced by Fe, the substitution of the following B is not independent but tends to take place near the first substituted boron. If, in this way, a clustering of iron atoms occurs due to preferred substitution, the result would be a weaker decrease in the 4 B neighborhood configurations than predicted by the fully random substitution calculation. Unfortunately, in the case of correlated substitution, no simple replacement exists for the algorithm used in our calculation.

It seems that the correlated substitution of B by Fe gives a natural explanation of the iron precipitation observed[10] as a first step in the crystallization of these glass alloys. We do not claim that these iron "clusters" are microcrystalline α-Fe, since their neighborhood is highly distorted; the Mossbauer experiment detects no disolved boron (i.e., less than 1 at.%) in the precipitated α-Fe (the linewidth, hyperfine field, and isomer shift is equal to that of pure Fe). The iron "clusters" due to correlated substitution of Fe may serve as nuclei for crystallization, i.e., their existance provides a possible microphysical explanation of the whole crystallization process.

An important distinction between the two models used lies in the B coordination number. In the quasicrystalline model it is exactly 9 while in the DRP model it is closer to 6. Unfortunately, no direct experimental verification of B coordination has been made because of the unique properties of the boron atom: its x-ray scattering cross section is very small, while its neutron inelastic scattering cross section is very high. The DRP models of Fe-B glass alloys do reproduce the diffraction data in considerable detail.[1] A more direct resolution of the question of B coordination would, therefore, be of significant value in resolving the nature of the structure of boron containing glasses.

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