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Short-range order in transition-metal—metalloid glasses

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Iron hyperfine-field distributions of amorphous Fe-B (15–25 at.% B) alloys were determined by the Mössbauer technique. They show the presence of a strongly correlated local order which can be described in the $Fe_{75}B_{25}$ glass as the chemical short-range order of the Fe_3B intermetallic compound.

The fundamentally interesting and technically attractive properties of metallic glasses are determined by their amorphous structure. Most of the experimental information on the structure is obtained from the interference function and radial distribution function (RDF) determined by x-ray, electron, and neutron scattering techniques. These functions characterize both the short-range and long-range order present in the glass. Despite many efforts[1] to develop three-dimensional models for atomic arrangements which are consistent with these experimental characterizations the description of the amorphous structure is far from being solved yet and the existence and nature of local order is open to question at present.

However, there is a possibility to obtain direct information on the nearest atomic neighborhoods using Mössbauer or NMR measurements.[2] In this article we will deal only with transition-metal—metalloid type amorphous alloys and as a model system the ferromagnetic Fe-B glasses were chosen. The aim of this paper is to show that strong local order exists in these alloys suggesting that their structure can be described as a locally distorted intermetallic-compound lattice.

The amorphous Fe-B samples were prepared by rapid quenching from the melt in the 15- to 25-at.% B concentration range. Their amorphous structure was verified by x-ray measurements. We have measured by Mössbauer effect the hyperfine-field distributions $p(H)$ of these glasses as a function of concentration. For the Mössbauer measurements a conventional constant-acceleration spectrometer was used with a Co^{57} in Pd source.

The Mössbauer spectra consist of six strongly broadened and overlapping lines characteristic of amorphous alloys. The evaluation of $p(H)$ from such spectra is a rather difficult task often hindered by systematical errors due to the overlap of the lines and to uncertainties in the intensities of the second and fifth lines caused by texture present in the sample. However, with a simple procedure[3] we can eliminate these difficulties. The intensity of the second and fifth lines ($\Delta m = 0$) depends strongly on the angle between the directions of the emitted γ rays and the magnetic moments in the sample. By using small permanent magnets the sample can be polarized almost completely in the plane of the ribbon and we can change the angle between the magnetization (i.e., the plane) and the γ direction. From two linear combinations of two spectra measured at different angles ($\approx 30°$ and $90°$, respectively) we obtain two subspectra, which separately contain the first, third, fourth, and sixth ($\Delta m = \pm 1$) and the second and fifth lines ($\Delta m = 0$) of the original spectra. From these subspectra, which are free from overlap, we can reliably determine $p(H)$ because of the possibility of self-consistency check. Following the method of Ref. 3, the $p(H)$ distribution was approximated by a binomial distribution whose shape was least-square fitted to the spectra and the effects of isomer-shift and quadrupole-splitting distributions were also taken into account. The results are shown in Fig. 1.

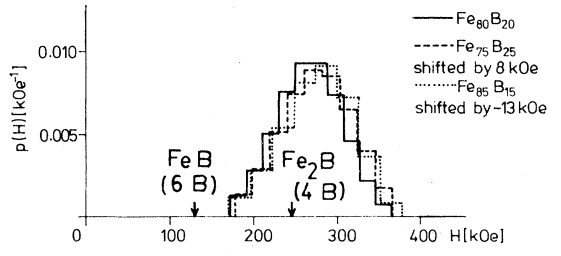

FIG. 1. Concentration dependence of the hyperfine-field distribution determined at 80 K. They are shifted by the difference in their average hyperfine-field value. The hyperfine-field values of FeB and Fe_2B are also shown.

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From these $p(H)$ distributions two main conclusions can be drawn: (i) The distributions are relatively narrow, the half-width of $p(H)$ in amorphous $Fe_{80}B_{20}$ is about $\Delta H \approx 45$ kOe. (ii) The distributions are rather insensitive to the change in the boron concentration as can be seen in Fig. 1. The linewidth of the amorphous $Fe_{85}B_{15}$ is about 1.6 mm/sec (while that of pure iron is about 0.2 mm/sec) and within the experimental error there is no extra broadening due to a further 10-at.% increase in the boron concentration.

These results can be compared with the predictions of the dense-random-packing (DRP) model of hard spheres which is generally accepted as a good first approximation for the structure of glassy alloys. In the amorphous Fe-B system Boudreaux has performed[4] careful calculations of the structure by DRP of spheres with different diameters using Lennard-Jones potential for the relaxation procedure. According to his results[4] the number of boron neighbors of an iron atom in the $Fe_{75}B_{25}$ alloy show a fluctuation $\Delta n_b \approx \pm 2$ around the average number, $\bar{n}_B = 2.15$. For decreasing boron concentration both $\bar{n}_B$ and Δn_B decrease, for example: in $Fe_{85}B_{15}$ these values are $\bar{n}_B = 1.13$ and $\Delta n_B \approx \pm 1$.

This narrowing of the boron distribution for decreasing metalloid concentration is just the general feature of *any* random model.

On the other hand, the iron hyperfine field depends sensitively on the number of nearest boron neighbors as can be seen from the comparison of different intermetallic compounds. In Fe_2B the Fe atoms have four B and 11 Fe nearest neighbors, their hyperfine field is 245 kOe, while in FeB the Fe atoms have six B and ten Fe nearest neighbors with a hyperfine field of 130 kOe.[5] We can compare these values with that of the Fe-III sites (four B and ten Fe neighbors) in the metastable Fe_3B compound.[6] Its hyperfine field is 230 kOe which agrees within 6% with the value taken from Fe_2B where the number and distance of iron atoms are different. On the other hand, the large difference in the hyperfine fields of FeB and Fe_2B shows the highly dominant effect of boron neighbors.

Consequently, the iron hyperfine-field distribution of the Fe-B glasses should narrow with decreasing boron concentration reflecting the before-mentioned narrowing of B distribution calculated[4] in DRP model, which is not found in our experiment.

Not only the concentration dependence of $p(H)$ but even the shape (as determined by the average value and width) at a given composition is quite different from the predictions of a DRP model. For example, the average iron hyperfine field in $Fe_{75}B_{25}$ would be expected to be about 300 kOe, the value of Fe-I sites (two B nearest neighbors) in Fe_3B. The measured value is 268 kOe, considerably lower and suggests a higher average boron coordination number. As it can be seen in Fig. 2, the observed width of $p(H)$ does not allow fluctuations larger than ± 1 in the number of surrounding nearest boron neighbors which is half of the value predicted by the DRP model. (The vertical lines in Fig. 2 show the measured hyperfine fields of Fe_3B corresponding to four B, three B, and two B neighborhood with increasing hyperfine field.)

Thus our results do not support the DRP model and suggest the presence of a strong local order in these amorphous alloys. Strong evidence was also shown for the chemical short-range order in $Pd_{78}Ge_{22}$ glass by recent extended x-ray absorption fine structure (EXAFS) measurements.[8] On the nature of the local order the study of crystallization gives valuable information.[9] It was found that the first step of the crystallization of the glassy material is the precipitation of α-Fe until the composition of the remaining glass reaches $Fe_{75}B_{25}$. In the second step this remaining glass transforms into Fe_3B intermetallic compound (which decomposes at higher temperatures into α-Fe and Fe_2B).

This sequence of crystallization (especially the privileged role of the 25-at.% B-glass composition) suggests a very strong correlation between the local structure of the Fe_3B intermetallic compound and that of the glasses in question, which is supported by the considerable similarity of their Mössbauer spectra (Fig. 3).

It seems to be natural to describe the glass structure as a locally distorted nonstoichiometric Fe_3B "quasicrystalline" structure. According to this concept the amorphous alloy can be described by a distribution of lattice parameters with a mean value of the

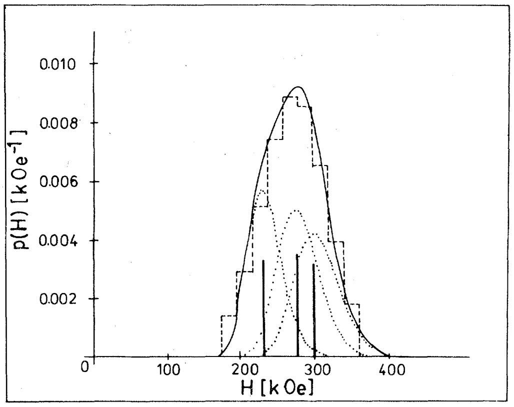

FIG. 2. Hyperfine-field distribution of the amorphous $Fe_{75}B_{25}$ alloy (dashed line) determined at 80 K. The full line is the calculated curve with a single free parameter as explained in the text.

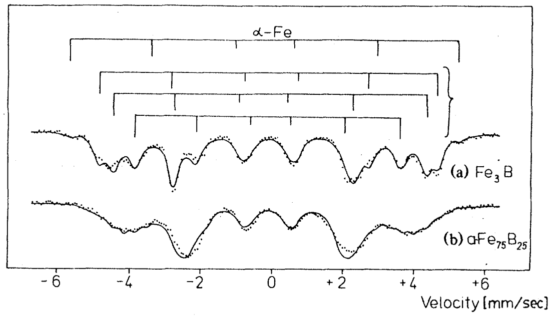

FIG. 3. (a) Room-temperature Mössbauer spectrum of Fe_3B obtained after the crystallization of the nominally $Fe_{75}B_{25}$ glass. The small off-stoichiometry (−0.4-at.% B) results in the precipitation of α-Fe as shown in the figure. The six-line patterns of Fe atoms with different environments are also indicated; the full line is the fitted curve. (b) Room-temperature Mössbauer spectrum of amorphous $Fe_{75}B_{25}$. The full line is the calculated curve with a single free parameter as explained in the text.

crystalline intermetallic compound, r_0 as

$$p(r) \sim \exp\left[-\frac{1}{2}\left(\frac{r-r_0}{\Delta r}\right)^2\right] ,$$

where the relative width of the distribution can be determined from the shape of the first peak of the radial distribution function measured by x-ray method. A similar description was suggested by Maitrepierre[10] for the structure of Fe-Pd-P and Ni-Pd-P glasses, based on the crystal structure of Pd_3P: the fluctuation of the interatomic distances was found to be about 8%. In a similar measurement $\Delta r/r_0 \approx 7.5\%$ ($r_0 = 2.61$ Å) was found for amorphous $Fe_{80}B_{20}$.[11] In this description long-range correlations are neglected but local properties such as hyperfine field can be successfully described. Because of the Gaussian broadening of the transition-metal—metalloid distance the discrete hyperfine-field value, H_0, characteristic for the intermetallic compound will be also broadened giving a hyperfine-field distribution around this value. The distribution is given by

$$p(H) \sim \exp\left[-\frac{1}{2}\left(\frac{H-H_0}{\Delta H}\right)^2\right] ,$$

where

$$\Delta H = \left(\frac{\partial H}{\partial r}\right)_{r_0} \Delta r .$$

The Mössbauer spectrum of the Fe_3B intermetallic compound can be satisfactorily described[6] by three six-line patterns as indicated in Fig. 3(a). (The Fe_3B was obtained by the crystallization of the nominally 25-at.% B glass, the real composition of which was determined from the amount of the precipitated α-Fe as 24.6-at.% B.) The small deviations between the calculated and measured curve can be attributed to a distribution of easy magnetization directions in the Fe_3B sample, as was found for Fe_3P.[6]

In Fig. 3 the vertical lines show the hyperfine-field values of these six-line patterns which characterize the Fe atoms with different environments in Fe_3B. The point-curves show the hyperfine-field distributions around these values caused by the fluctuation of the transition-metal—metalloid distance. It was assumed in this calculation that the broadening of the discrete hyperfine-field values is simply proportional to the hyperfine fields. The full line shows the sum of these elementary distributions which is characterized by a *single* parameter: the half-width of the distribution around the highest Fe_3B hyperfine field, ΔH_0. The measured $p(H)$ of the amorphous $Fe_{75}B_{25}$ alloy (dashed line) agrees rather well with the calculated curve, with $\Delta H_0 = 31$ kOe. In Fig. 3(b) the full line is the curve calculated in this model (again only the single parameter ΔH_0 was used). The deviations from the measured spectrum are caused by the use of the discrete isomer shift and quadrupole splitting values of Fe_3B instead of any assumptions for the unknown distributions in the glass. A similarly good description can be obtained with the assumption of equally broadened elementary distributions (in this case $\Delta H = 29$ kOe). In the absence of measured $(\partial H/\partial r)_{r_0}$ the transformation of ΔH into Δr is rather arbitrary.

It seems that the most essential feature of this model is the use of the hyperfine fields of Fe_3B around which the elementary distributions are centered. The insensitivity of the $p(H)$ shapes for boron concentration (less than 25-at.% B) is also connected with this Fe_3B structure where the excess iron atoms will occupy the boron sites. Their hyperfine field will be on the high-field side of the distribution (although the exact values are not known) while a decrease is expected in the intensity of the low-field component due to decrease in the number of iron atoms with given number of boron neighbors. On the whole, these changes will result mainly in a small shift of the distributions (the observed increase in the average values is less than 10%).

By generalizing the fairly good description of the amorphous $Fe_{75}B_{25}$ alloy in the framework of the "quasicrystalline" model (which involves only a single parameter), we suggest that the complex structure of the amorphous transition-metal—metalloid alloys at arbitrary composition is determined by two dominant contributions, namely, (i) structural disorder, and (ii) chemical disorder.

In our terminology, structural disorder means the commonly used "amorphous" idea, i.e., the local distortion of the corresponding intermetallic compound [in our case $T_{75}X_{25}$ (T is a transition metal and X is a metalloid)] which can be characterized by a distribution of its lattice parameter. The width of this fluctuation in the investigated cases is less than 10%.

The idea of chemical disorder immediately presumes the existence of a privileged composition (in our case 25-at.% metalloid content) of the intermetallic compound which serves as the basis for the glass structure. Then any deviation from this composition, or the substitution of more components means a distortion of the "ideal" amorphous structure in analogy to the case of nonstoichiometric intermetallic compounds, i.e., there are sublattices (transition metal or metalloid) which remain unchanged due to the preferred substitution of atoms. Most of the physical properties of amorphous alloys seem to be dominated by this off-stoichiometry, similarly to the case of crystalline alloys.

The basic difference between our chemically correlated model and the dense random packing (DRP) of hard spheres[1,4,12] (generally accepted as a good model for the structure of glassy alloys) is the existence of fixed coordinations (i.e., "sublattices") of the transition metals and metalloids in the former model which results in a much stronger correlated structure than predicted by the DRP models.

Generally, in amorphous alloys apart from privileged compositions, we observe the effects of both the structural and chemical disorder. Thus the interpretation of their properties is masked, and carefully planned experiments are necessary to obtain reliable information on the real effect of amorphousness.

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[1] G. S. Cargill, III, *Solid State Physics* (Academic, New York, 1975), Vol. 30, p. 227.

[2] J. Durand and M. F. Lapierre, J. Phys. F 6, 1185 (1976); K. Raj, A. Amamou, J. Durand, J. I. Budnick, and R. Hasegawa, in *Amorphous Magnetism II,* edited by R. A. Levy and R. Hasegawa (Plenum, New York, 1977), p. 221; J. Durand and M. Yung, *ibid.,* p. 275; K. Raj, J. Durand, J. I. Budnick, C. C. Tsuei, and S. Skalski, Solid State Commun. 24, 189 (1977).

[3] I. Vincze, Solid State Commun. 25, 689 (1978).

[4] D. S. Boudreaux, Phys. Rev. B 18, 4039 (1978).

[5] L. Takács, M. C. Cadeville, and I. Vincze, J. Phys. F 5, 800 (1975).

[6] According to recent x-ray and Mössbauer measurements (Ref. 7) the metastable Fe_3B obtained from the crystallization of Fe-B glasses has a tetragonal lattice, isostructural to Fe_3P, E. Lisher, C. Wilkinson, T. Ericson, L. Hägström, L. Lundgren, and R. Wäpling, J. Phys. C 7, 1344 (1974). In this structure there are three crystallographically inequivalent Fe sites with the same relative occupation, namely, Fe-I (two B and 12 Fe), Fe-II (three B and ten Fe), and Fe-III (four B and ten Fe) with 300-, 275-, and 230-kOe hyperfine fields, respectively.

[7] H. Franke, U. Herold, U. Köster, and M. Rosenberg, in *Third International Conference on Rapidly Quenched Metals, Brighton, England, 3-7 July 1978* (The Metals Society, London, 1979), Vol. 1, p. 155; J. L. Walter, S. F. Bartram, and I. Mella, Mater. Sci. Eng. 36, 193 (1978); U. Herold and U. Köster, Z. Metallk. 69, 326 (1978). These results are quite different from that of W. K. Choo and R. Kaplow, Metall. Trans. A 8, 417 (1977), obtained on splat-cooled samples with low B content.

[8] T. Hayes, J. W. Allen, J. Tauc, B. C. Giessen, and J. J. Hauser, Phys. Rev. Lett. 40, 1282 (1978).

[9] T. Kemény, I. Vincze, B. Fogarassy, and S. Arajs, Phys. Rev. B 20, 476 (1979).

[10] P. L. Maitrepierre, J. Appl. Phys. 40, 4826 (1969).

[11] F. Hajdu (private communication).

[12] G. S. Cargil, III, J. Appl. Phys. 41, 2248 (1970); C. H. Bennett, J. Appl. Phys. 43, 2727 (1972); D. E. Polk, Acta Metall. 20, 485 (1972); J. F. Sadoc, J. Dixmier, and A. Guinier, J. Non-Cryst. Solids 12, 46 (1973); J. L. Finney, Nature 266, 309 (1977); D. S. Boudreaux and J. M.-Gregor, J. Appl. Phys. 48, 152, 5057 (1977).