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Structure and crystallization of Fe-B metallic glasses

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The structure and crystallization of amorphous $Fe_{1-x}B_x$ ($0.12 < x < 0.25$) alloys have been investigated by Mössbauer spectroscopy, differential scanning calorimetry and magnetization measurements. It was found that the first step in crystallization 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 the Fe_3B intermetallic compound which decomposes at higher temperatures into α-Fe and Fe_2B. The results support a quasicrystalline model, where the structure of Fe-B glasses is based on a locally distorted off-stoichiometric Fe_3B lattice.

I. INTRODUCTION

During recent years the glassy alloys have appeared as a new class of metallic materials. The understanding of the structure and the thermal stability of these essentially metastable materials is of great importance from both the fundamental and practical viewpoints. In this paper we present new results concerning the Fe-B system. The structure of the alloys in the glassy and crystalline forms has been investigated with Mössbauer spectroscopy. The transition from the glassy to the crystalline state has been studied using a differential scanning calorimeter (DSC) and a vibrating sample magnetometer (VSM). The results of our investigations, which may also be relevent to other transition-metal–metalloid systems, are described below.

It is frequently claimed that as a first approximation the structure of the metallic glasses can be described by the dense random packing of hard spheres (DRPHS).[1] The work "random" is used here only in restricted sense. Reasonable agreement with experiments can hardly be achieved without supposing the absence of nearest-neighbor metalloid pairs.[2]

The glass transition in a hard-sphere system has been studied by two independent computer experiments.[3,4] Both studies indicate qualitative differences between the hard-sphere results and the experimental data. A computer-simulated system of hard spheres does not show the heat-capacity jump at the glass-transition temperature, T_g.[4] Furthermore, the configurational entropy of the glassy state remains of the order of the melting entropy[3] in clear contradiction with experimental results.[5] Gordon *et al.*[3] emphasize that a similar kind of discrepancy is found in the theory of liquids. It appears that the concepts which seem to be relevant for structural analysis cannot be used for explaining the stability of the glassy materials. The structure is determined mainly by repulsive interactions. However, the stability is controlled by attractive forces, i.e., bonding.[6] The chemical bonding plays also an important role in the formation of metallic glasses. Thus, a quasichemical theory of pair interactions[7] can explain the main tendencies such as easy glass formation by eutectic compositions.

The thermal stability of different glassy alloys has been investigated by Masumoto and co-workers.[2,8] According to their work, the crystallites of the main metallic component (I) precipitate from the noncrystalline matrix when the material is heat treated slightly above T_g. At higher temperature the remaining glass crystallizes in a complex ordered phase of metal and metalloid (II). According to the past studies the metastable intermetallic compounds are considerably different from the stable crystalline phases.

The appearance of the II phase means that there is an intermetallic crystalline compound which can be attained by the glass at temperatures lower than those needed for the creation of stable phases. One can assume that the formation of II crystals requires only a small reordering of the glass. In this case the II structure would be the natural building element of the glass structure. Instead of DRPHS construction, the glass should be imagined as a locally distorted nonstoichiometric II quasicrystalline structure. For example, the important role of Pd_3P in the structure of the Pd-Ni-P and Pd-Fe-P amorphous alloys has been emphasized by Maitrepierre.[9] Obviously, more work is needed for elucidating the problems of structure and thermal stability. Specifically, further experimental investigations should include the following considerations.

First, the structure and thermal stability of the glasses should be investigated in the same system and in the widest possible range of metalloid concentration.

Second, the II phase which plays a central role in the problem should be identified. The Fe-B system fulfills both above requirements. Fukamichi *et al.*[10] and Ray *et al.*[11] have shown that glassy alloys containing 9–27-at.% B can be prepared by rapid quenching techniques. Furthermore, Hasegawa *et al.*,[12] using $Fe_{80}B_{20}$ (Metglas 2605), have found that the II phase in this material is Fe_3B metastable intermetallic compound.

Third, as the local structure of glasses and metastable crystalline alloys seem to be very important, an experimental method should be selected which is very sensitive to the nearest-neighbor environment. Mössbauer spectroscopy is particularly adequate for this purpose.

Fourth, for a meaningful comparison with structural investigations, quantitative characteristics of thermal stability should be measured. In addition to the knowledge of crystallization temperatures reported by Fukamichi *et al.*[10] and Ray *et al.*,[11] data are also needed for the enthalpy change, the thermal activation energy and the kinetic law describing the crystallization process. These properties can be measured conveniently by DSC. The appearance and decomposition of magnetic phases can also be followed by VSM.

II. EXPERIMENTAL

A. Sample preparation

The alloys which we have investigated have been prepared in three different laboratories. The alloy labeled as Mg 2605, having the nominal composition of $Fe_{80}B_{20}$, was purchased from the Allied Chemical Co., Morristown, N.J. The series of glassy materials designated by BL has been prepared from the melt in ribbon form using a centrifugal-spinning technique.[13] The alloys coded as CRIP have been prepared in the Central Research Institute for Physics, Budapest, by quenching to the external surface of a rotating copper disk.[14] Takahashi and Koshimura[15] have reported that glassy Fe-B alloys can be formed only by means of a rotating steel disk. In our laboratory we have found that by optimizing the experimental parameters of the apparatus (disk diameter, pressure, temperature of melt, revolution speed, etc.) it is also possible to prepare glassy Fe-B alloys with a copper disk.

B. Mössbauer spectroscopy

For the Mössbauer measurements a conventional constant-acceleration spectrometer was used. The measurements were carried out at room and at liquid-nitrogen temperatures. The Mössbauer spectra of the crystalline phases were evaluated

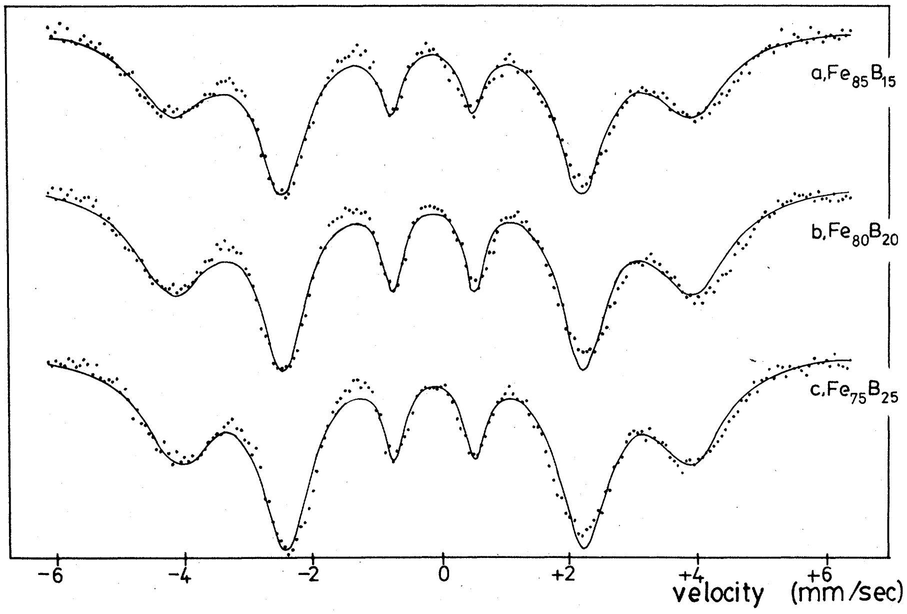

FIG. 1. Measured room-temperature Mössbauer spectra of three metallic glasses produced by Bell Laboratories (dots). Continuous line: fitting with average parameters.

using the conventional procedure of fitting six-line patterns to the measured spectra. Some typical spectra of the amorphous alloys are shown in Fig. 1. The most characteristic feature of these spectra is the absence of structure: they consist of six strongly broadened and overlapping lines. For example, the linewidth of the outer lines is about 1.5–1.6 mm/sec which is more than five times larger than that of the source. The strong line broadening reflects fluctuations in the strength of the hyperfine interaction resulting from different environments. These spectra can be described by the distribution of hyperfine fields, isomer shifts, and quadrupole splittings whose evaluation is a rather difficult task. A common simplification for the extraction of the average hyperfine field $\overline{H}_{\mathrm{Fe}}$ and the average isomer shift $\langle \mathrm{IS} \rangle$ from such spectra is the fitting of a six-line pattern with different widths for the three pairs of lines.[16–19] The continuous line in Fig. 1 has been fitted this way. The deviations between the measured and calculated curves show that this type of analysis, though widely used, can cause significant systematical errors, especially when the hyperfine field distributions are strongly asymmetric.

The problems associated with overlapping lines can be eliminated by a simple procedure described elsewhere.[20] The intensity of the second and fifth lines of the Mössbauer spectra depends strongly on the angle between the directions of the emitted γ rays and the magnetic moments in the sample. From the linear combination of two spectra measured at different angles, we obtain two subspectra, which separately contain the 1-3-4-6 and the 2-5 lines of the original spectrum. The 2-5 subspectra, separated from the spectra of Fig. 1, are shown in Fig. 2.

As the subspectra are free from overlap, the hyperfine-field distribution $p(H)$ can be determined reliably. Following the method of a previous paper,[20] we have approximated $p(H)$ by binomial distribution:

$$p^z_{\mathrm{bin}}(k) = \binom{z}{k} y^k (1-y)^{z-k}, \quad k = 0, 1, \ldots, z\,. \tag{1}$$

The probability histogram can be determined from

$$p\big(H(k) < H < H(k+1)\big) = p^z_{\mathrm{bin}}(k)/\Delta H\,, \tag{2}$$

where

$$H(k) = H_0 + k\Delta H\,. \tag{3}$$

The parameters, H_0, ΔH, and y can be calculated from the least-squares fitting of the spectra. As the shape of the binomial distribution is determined by the freely fitted y parameter, the procedure has clear advantages over the fitting with an arbitrarily chosen distribution such as Lorentzian or Gaussian. The only arbitrarily selected parameter is z which determines the smoothness of the $p(H)$ distribution. We used $z = 20$, but the spectra can be described equally well with any $z \geqslant 6$ value. The continuous line of Fig. 2 shows the fitted curve which is in good coincidence with the measured spectra. In our description, z is an arbitrary integer and y is a fitted parameter characteristic of the shape of the distribution. They are not related to the coordination number and metalloid concentration.

Previously, Fujita *et al.*[21] fitted the Mössbauer spectrum of amorphous $\mathrm{Fe}_{80}\mathrm{P}_{17}\mathrm{C}_3$ assuming bcc-type binomial distributions of nearest-neighbor configurations (i.e., the coordination shells were characterized by $z_1 = 8$ and $z_2 = 6$, respectively, while $y = 0.2$ was supposed to be the concentration of metalloid atoms). From this analysis, they deduced the existence of bcc-type short-range order in the glassy state. However, as the z parameters can

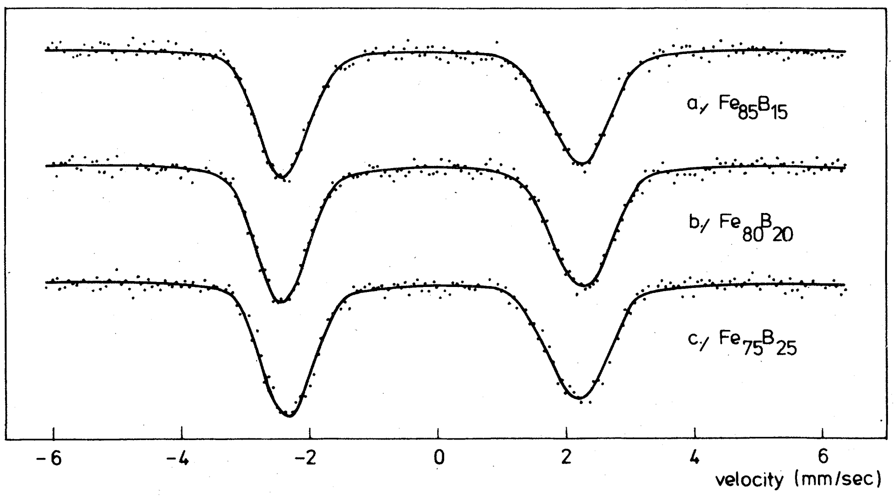

FIG. 2. Separated peaks 2-5 of the spectra shown in Fig. 1 fitted with the determined hyperfine-field distribution.

be chosen[20] quite arbitrarily, our results do not support the conclusion of Fujita *et al.*[21]

C. Differential scanning calorimetry

A Perkin-Elmer-type DSC-2 calorimeter has been used for investigating the thermal properties. The theory[22–24] and practice[25] of DSC is well known. We followed the usual procedure of calibrating measured temperature and energy values with the melting point and latent heat of In, Pb, Zn, and K_2CrO_4.

The temperature correction is especially important for studies of the kinetics of transformations.[26,27] Richardson and Savill have shown[28] that the temperature calibration with melting point standards is correct, while the temperature lag inside the sample is much smaller than that between the sample and thermometer. The condition is undoubtedly fulfilled in our case. In addition to the steady-state temperature correction discussed above, there is an extra term due to the transformation itself. It is usually negligible on account of the small value of instrumental heat resistance. However, in the case of a highly exothermic reaction such as crystallization, the systematic error can be significant. Our practice has shown that for a 2–5-mg metallic glass sample, crystallized with a heating rate of 10 K/min, $\Delta T_{\mathrm{syst}} \lesssim 0.5$ K, i.e., the order of instrumental temperature inaccuracy. Following the ideas of Heuval and Lind,[29] a computerized temperature correction procedure has been applied,[30] which proved to be reliable even at heating rates larger than 10 K/min. Nevertheless, the data published in this paper are restricted to 0.31–10 K/min heating rates.

The problems of nonisothermal investigation of solid-state reactions have been reviewed by Flynn and Wall[31] and Sestak and Berggren.[32] It has been shown[33] that an apparent activation energy $E_a^{(C_0)}$ can be determined for each arbitrarily fixed transformed fraction C_0 from the heating rate, v, dependence of the temperature values belonging to C_0, T_{C_0}, and v. When $E_a^{(C_0)}$, which is proportional to the slope of the $[T_{C_0}(v)]^{-1}$ vs $\ln v$ plot, is independent from C_0, an apparent activation energy can be defined. Ozawa has demonstrated[34] that in this case dynamic and isothermal measurements can be mapped to each other. Sestak and Berggren[32] have discussed the applicability of theoretical models, originally devised for isothermal processes, to dynamic measurements.

It has been demonstrated by isothermal measurements[35–40] that the time, t, dependence of the crystalline fraction C in metallic glasses follows the Johnson-Mehl-Avrami equation[41]

$$C = 1 - \exp\{-[k(T)t]^n\}\,, \tag{4}$$

where the rate factor is usually approximated by an Arrhenius-type temperature, T, dependence

$$k(T) = k_0 \exp(-E_a/k_B T)\,, \tag{5}$$

where k_B is the Boltzmann constant, E_a is the apparent thermal activation energy, and k_0 is the frequency factor. The quantity n is the characteristic exponent. Using the differential form of Eq. (4),[32]

$$\frac{dC}{dt} = k_0\left[\exp\left(-\frac{E_a}{k_B T}\right)\right](1 - C)[-\ln(1 - C)]^{(n-1)/n}\,, \tag{6}$$

the kinetic parameters can be determined from a series of dynamic measurements made with different heating rates.

D. Static magnetic measurements

The magnetic behavior of Fe-B alloys has been determined as a function of temperature between 300 and 900 K. These measurements have been made using a VSM Princeton Applied Research Corp. (Model FM-1*D*).[42] The magnetometer was calibrated by means of a polycrystalline high-purity Fe sphere using the slope method described elsewhere.[43,44] The temperature of the sample was determined by a Chromel-Alumel thermocouple. The absolute temperatures stated in this paper associated with magnetization plots are correct to ±2 K.

From magnetization measurements, one can determine the Curie point[45,46] and can get some insight to the crystallization behavior.[12,15,46–49]

III. RESULTS AND DISCUSSION

A. Structural investigations of glasses

The structure of metallic glasses is usually described by radial distribution functions. As the parameters of the Mössbauer spectrum depend quite sensitively on nearest- and next-nearest-neighbor environments, structural information can be obtained from the probability distribution of spectrum characteristics. We will discuss here mainly hyperfine-field distributions.

The concentration dependence of the average parameters can be seen in Fig. 3. The relatively great systematic error is estimated by comparing the results of several equally well-justified fitting hypotheses. Taking into account these significant systematic errors, the general trends are in good agreement with previously published data on Fe-B.[50]

The hyperfine field decreases with increasing metalloid concentration. It is quite consistent with the decrease in the magnetic moment of Fe atoms

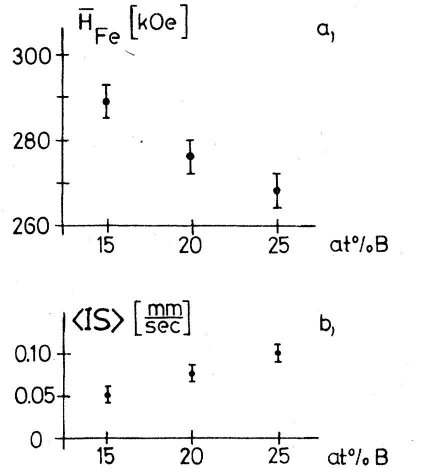

FIG. 3. Concentration dependence of average hyperfine field ($\bar{H}_{Fe}$) and isomer shift ($\langle IS \rangle_{Fe}$) determined at 80 K.

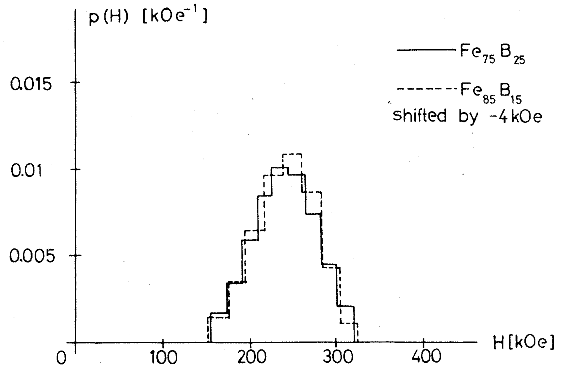

FIG. 4. Room-temperature hyperfine-field distributions determined from the fitting of overlap-free subspectra. The $p(H)$ of the $Fe_{85}B_{15}$ glass is shifted by the difference between $\bar{H}_{Fe}$ values.

reported by Fukamichi *et al.*[10] and Hiroyoshi *et al.*[51] from magnetic measurements. The hyperfine field is found to be nearly proportional to the magnetic moment of Fe in intermetallic compounds[52-54] and in metallic glasses.[55,56] The effect of the Fe moment, μ_{Fe}, can be separated in systems where two transition metals could contribute to the average magnetization, $\bar{\mu}$. In crystalline binary alloys such as Fe-Ni or Fe-Co the hyperfine field is usually described[57] as

$$\bar{H}_{Fe} = H_{CP} + H_{CEP} = A\mu_{Fe} + B\bar{\mu} , \qquad (7)$$

where the contributions from conduction-electron polarization (CEP), H_{CEP}, and core polarization, H_{CP}, are comparable to each other. The significant decrease of the CEP contribution in intermetallic compounds and metallic glasses would indicate a dominant p character of the s-p hybridized conduction band in these materials.

The magnetic properties are usually interpreted by the donor model. In this concept, the decrease of the transition-metal moment is explained[16,58-60] by the transfer of excess electrons supplied by the metalloid to the empty d orbits of the transition metal. The amount of charge supposed to be transferred from boron to iron can be determined from the magnetic properties of the existing intermetallic compounds, i.e., Fe_2B and FeB.[16,53] It gives 1.6 electron/(B atom) for the amount of transferred charge. The change of Fe moment, in units of Bohr magnetors (μ_B), can also be determined from the measured[10,51] magnetization of Fe-B glasses, $d\mu_{Fe}/dC_B \approx -0.9\mu_B/(\text{B at.\%})$, where c_B is the boron concentration in at.%, which implies a donated electron number less than 0.8 electron/(B atom). This quite significant discrepancy makes the applicability of donor model questionable.

The main effect of metalloid admixture can be described by the hybridization between the s-d-type electron band of transition metals and the s-p orbitals of the metalloid. It results in a decrease of magnetic splitting of spin-up and spin-down subbands, i.e., a decrease in the magnetic moment and hyperfine field and only minor changes in the isomer shift. The significant decrease of the contribution of neighboring sites to the hyperfine field (CEP) both in glassy alloys and intermetallic compounds compared with that of binary crystalline alloys is very remarkable.

The hyperfine-field distribution has been determined from the 2-5 subspectra of Fig. 2. The results are shown in Fig. 4. The shape and width of the distribution is nearly independent of concentration. (The distribution for the 20-at.% B glass is not shown, because it is practically coincident with the average of the two other alloys.)

Both the relatively narrow hyperfine field distributions and their insensitivity to concentration changes suggest a strongly correlated structure for these glasses and disagree[61] with the expectations of the DRPHS model. Very recently Boudreaux[62] has carefully considered this model for the Fe-B system and, according to his calculations, the number of metalloid nearest neighbors shows a rather large, 0–5 B scatter, which increases for increasing B concentration. This increase would result in a broadening of the hyperfine field distribution, contrary to the observed results.

In Sec. III C we discuss the structure of the metastable intermetallic compound Fe_3B, which appears in the crystallization process of amorphous Fe-B alloys. The hyperfine field distribution of the $Fe_{75}B_{25}$ glass can be analyzed perfectly[61] with a single parameter: the relative width of the Gaussian broadening of the discrete hyperfine-field values found in Fe_3B intermetallic compound. This means that the local environment of a Fe atom is very similar in the crystalline intermetallic compound and in the glass. The loss of crystalline regularity in the glass can be described with $\Delta r/r_0$, which measures the characteristic average distortion of the Fe_3B cell in the Fe-B glasses. The value of this fluctuation in the atomic distances was determined from diffraction measurements. The width of the first peak of the radial distribution function in the MG 2605 alloy measured by the x-ray method is $\Delta r/r_0 = 7.5\%$ with $r_0 = 0.26$ nm.[63]

B. Thermal relaxation in the glassy state

In a strict thermodynamic sense, the real glassy state is unstable.[64] The apparent stability is caused by kinetic restrictions. As the kinetic constraints are relaxed (i.e., temperature increases), the noncrystalline material can decrease its volume and heat content even in the glassy phase. This relaxation has been observed recently in Pd-based metallic glasses by Chen and Coleman.[65] As the Fe-based alloys do not show a glass transition on heating, the sensitivity of our thermal measurements is not adequate for the quantitative measurement of thermal relaxation. Some effects of this phenomenon can nevertheless be detected in our magnetic measurements.

The static magnetization has been measured with increasing and decreasing temperatures using the rate of the temperature change of 2 K/min. The applied magnetic field H_a was 100 Oe (7.96×10^3 A/m). A small section of the amorphous metal strip was placed in the sample holder of the magnetometer in such a way that the plane of the strip was parallel to the magnetic field. Because of the smallness of the sample, the magnetization σ is expressed in arbitrary units.

Under these experimental conditions, the σ vs T plot below the Curie temperature T_C should be a straight line with zero slope. At some temperature T_t slightly below T_C, σ should rapidly decrease with increasing T. The kink point[45] occurring at T_t results from a transition from a nonuniform state of magnetization to a uniform one. As $H_a \to 0$, $T_t \to T_C$. For practical purposes, σ measurements in the small applied fields mentioned above should exhibit a kink-point behavior at T_t, which, within a few tenths of a degree Kelvin, can be taken as T_C.

Recently, it has been demonstrated[46] using $Fe_{40}Ni_{40}P_{14}B_6$ ($T_C = 520$ K) that the kink-point method is completely equivalent to the parabolic extrapolation from the Arrott-Kouvel-Belov (AKB) plots.[66-68] For this material the kink points are sharp and well defined. If the material undergoes considerable thermal relaxation, the kink points become "smeared out" and less sharp.[69] Figures 5 and 6 show that the above ideas are also applicable to the Fe-B series. The kink points are quite rounded. However, the quantity T_C can be easily

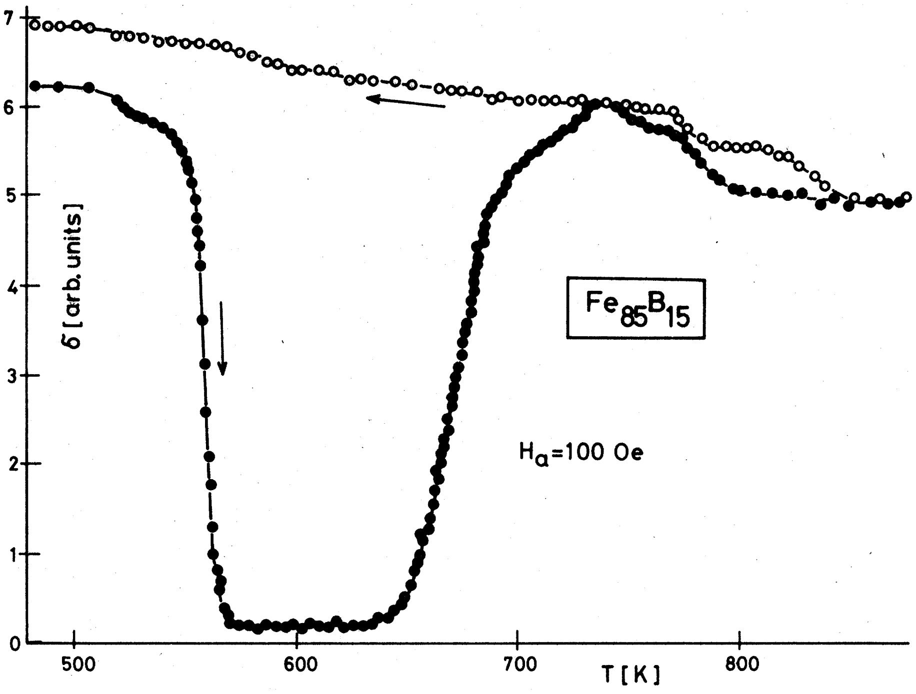

FIG. 5. Magnetization for $Fe_{85}B_{15}$ (BL) sample as a function of temperature in $H_a = 100$ Oe.

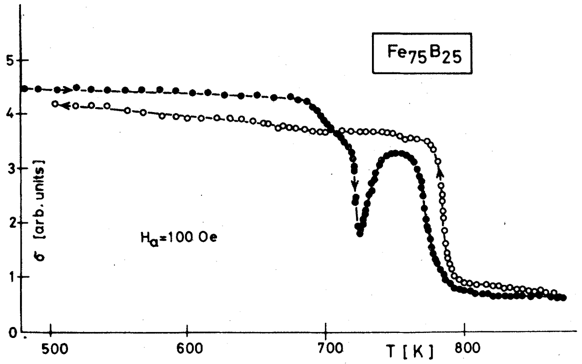

FIG. 6. Magnetization for $Fe_{75}B_{25}$ (BL) sample as a function of temperature in $H_a = 100$ Oe.

determined as the temperature at which σ decreases very rapidly with increasing T. The concentration dependence of T_C is shown in Fig. 7. Since the glassy alloys are unstable materials, it can be expected that such a conventionally intrinsic parameter as T_C would depend on the thermal history of the glass. This, indeed, is the case with numerous glassy systems. For example, Chen *et al.*[70,71] have clearly demonstrated that T_C can change with annealing temperature. Our data of T_C have been measured on "as-received" samples using the heating rate of 2 K/min. Figure 7 also presents values of T_C provided by Chen.[72] The agreement between his (triangles) and our (circles) values is excellent. The increase of T_C with increasing B concentration has also been reported by Takahashi and Koshimura[15] and Fukamichi *et al.*[10]

C. Crystallization

The transformation from the glassy to crystalline state has been investigated with differential scanning calorimetry, Mössbauer spectroscopy, and static magnetization measurements. Two typical DSC measurements of the crystallization rate can be seen in Figs. 8 and 9.

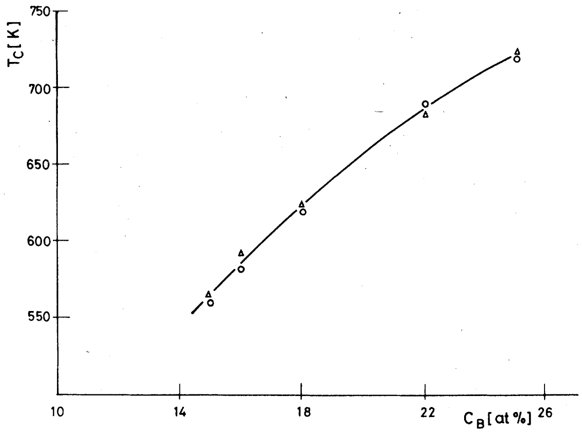

FIG. 7. Ferromagnetic Curie temperature as a function of B concentration (BL alloys).

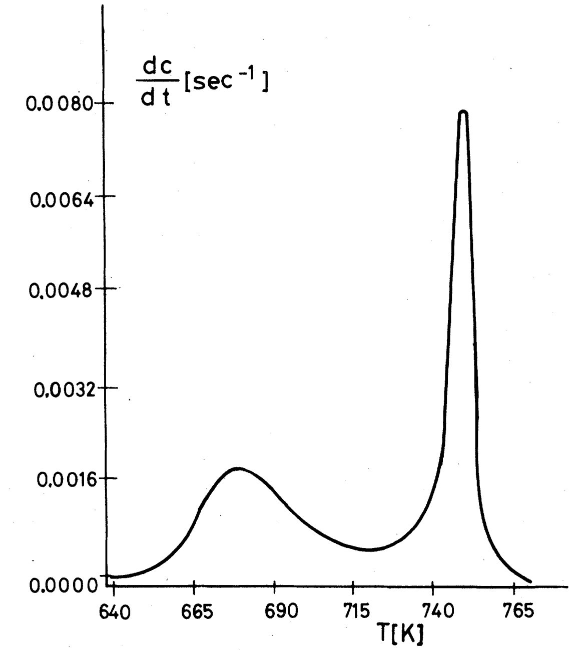

FIG. 8. Temperature dependence of the crystallization rate of $Fe_{85}B_{15}$ (BL) metallic glass.

The double crystallization given in Fig. 8 is characteristic of the glasses with relatively low B content, $c_B < 16$ at.%. The results of static magnetization measurements are shown in Figs. 5 and

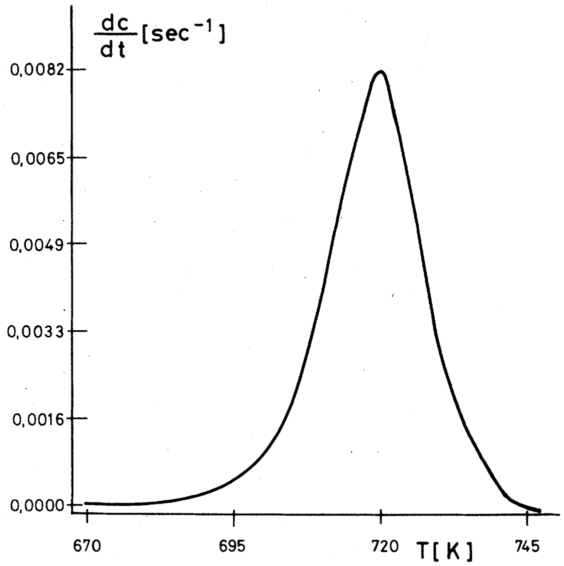

FIG. 9. Temperature dependence of the crystallization rate of $Fe_{80}B_{20}$ (BL) metallic glass.

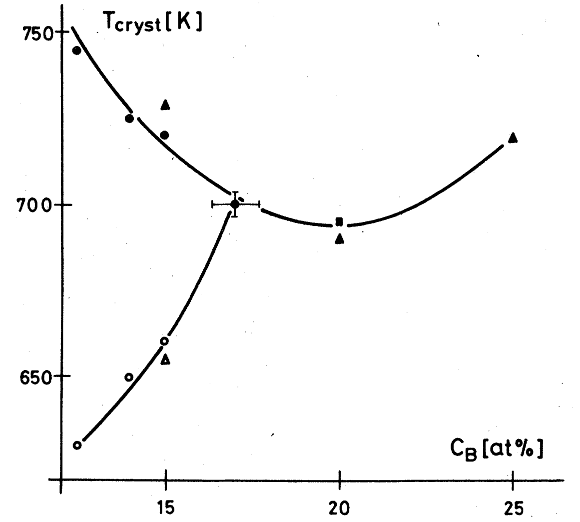

FIG. 10. Concentration dependence of the start temperature of different transformation stages. Open symbols correspond to the first stage: ●, ○: CRIP samples; ▲, △: BL samples; ■: MG 2605.

6. The increase of magnetization with increasing temperature above T_C results from the onset of crystallization. Two fairly well-resolved steps are evident in Fig. 5 (BL 15-at.%-B alloy), while the alloys with higher B content crystallize in a single-step process (see Fig. 6). A similar switchover between single and double state transformation with metalloid concentration has been observed in the Pd-Si system by Lewis and Davies[73] and in the Co-B-Si system by Funakoshi *et al.*[74]

In order to investigate the concentration dependence of thermal stability, we have plotted in Fig. 10 the continuous-heating start temperature of crystallization (Boswell[75]) observed by DSC with a 10-K/min heating rate. The same concentration dependence of thermal stability can be determined from magnetization measurements. The transformation behavior in the different concentration regimes will be discussed below.

The Mössbauer spectrum of $Fe_{85}B_{15}$ alloy, heat treated up to the end of the first transformation step, can be seen in Fig. 11(a). Subtracting the α-Fe contribution, the spectrum shown by Fig. 11(b) can be separated. The broad and featureless spectrum is characteristic of the remaining glass.

As the concentration dependence of the average hyperfine field and isomer shift is well known (Fig. 3), it can be used for the analysis of the remaining glassy phase. The parameters, measured at $T = 80$ K, should be compared because they are free from the errors caused by the concentration dependence of the Curie point. The average hyperfine field of the remaining glass is 268± 4 kOe in good agreement with that of amorphous $Fe_{75}B_{25}$ alloy. As the errors are mainly systematic ones, the parameters evaluated in the same way from similar spectra can be compared with greater precision. One can conclude that the B concentration of the glassy phase after the first stage of crystallization is $c_B = (25 \pm 1)$ at.%. Approximately the same composition can be determined from the precipitated amount of α-Fe.

The Mössbauer spectra of several Fe-B alloys can be observed in Fig. 12 after measuring the crystallization in the calorimeter. Besides α-Fe, a second phase can be detected which is clearly different from the equilibrium phase, Fe_2B (see Fig. 13). From the disappearance of the α-Fe contribution as composition approaches $Fe_{75}B_{25}$, it is concluded that the new phase is Fe_3B. The temperature dependence of the hyperfine fields in the crystallized $Fe_{75}B_{25}$ alloy spectrum [see Fig. 12(c)] does prove the occurrence of a single crystalline phase with inequivalent Fe sites. The results of our static magnetic measurements of the BL 25-at.%-B sample are presented in Fig. 6.

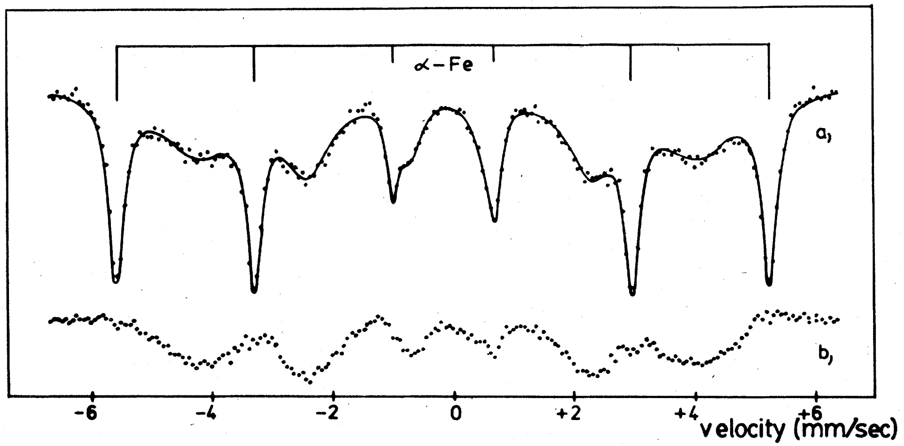

FIG. 11. (a) Room-temperature Mössbauer spectrum of the $Fe_{85}B_{15}$ (CRIP) alloy, heat treated to the end of the first stage of transformation. (b) The spectrum of the remaining glass, determined by subtracting the α-Fe contribution from the previous spectrum.

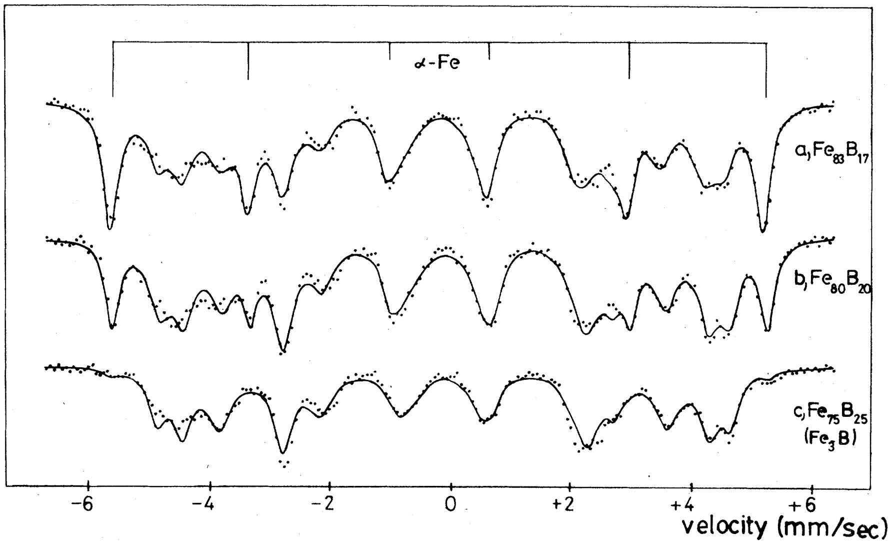

FIG. 12. Room-temperature Mössbauer spectra of several Fe-B alloys heat treated to the metastable crystalline state.

Above the clearly indicated T_C of Fe_3B the magnetization decreases to small values, showing that the amount of other magnetic phases is negligible.

The well-resolved Mössbauer spectrum of almost pure Fe_3B permits some new predictions concerning its crystal structure, which contradict the Mössbauer results of Choo and Kaplow[76] and question the identification of Fe_3B lattice with cementite. As is evident from Fig. 12(c), the Mössbauer spectrum of Fe_3B is quite complex and significantly different from that of the cementite.[77] The Fe_3B spectrum can be approximately described with the fitting of three six-line patterns. The use of greater numbers of six-line patterns does not result in a qualitatively better fit.

The three six-line patterns correspond to three different Fe sites, Fe(1), Fe(2) and Fe(3), respectively, the relative occupations of which are approximately 1 : 1 : 1. The Mössbauer parameters of the Fe(3) sites nearly agree with those of Fe_2B.[54] Thus, the nearest-neighbor environment has to be the same, i.e., these Fe atoms have four B neighbors.

In the cementite structure[77] there are two crystallographically inequivalent Fe sites, Fe(1) and Fe(2), which are coordinated by two C and three C first neighbors, respectively, the relative occupation of these sites being 1 : 2.

It can be concluded that the crystal structure of Fe_3B is significantly different from cementite, since both the metalloid coordination and relative ratio of inequivalent sites are quite different. The Mössbauer spectrum of Fe_3B can be explained by a tetragonal Fe_3P-type structure as was suggested very recently by several investigators.[78] In this identification the three different Fe sites correspond to local environments with two, three, and four B nearest neighbors.

The sequence of transformations in the double-stage processes ($12.5 < c_B < 16$ at.%) is well understood. The first step is the precipitation of α-Fe and the next one is the crystallization of the Fe_3B metastable intermetallic compound. The equilibrium state of the Fe-B system is the mixture of α-Fe and Fe_2B crystallites. The transformation of Fe_3B to the equilibrium phases has been observed by Hasegawa *et al.*[14] in magnetization mea-

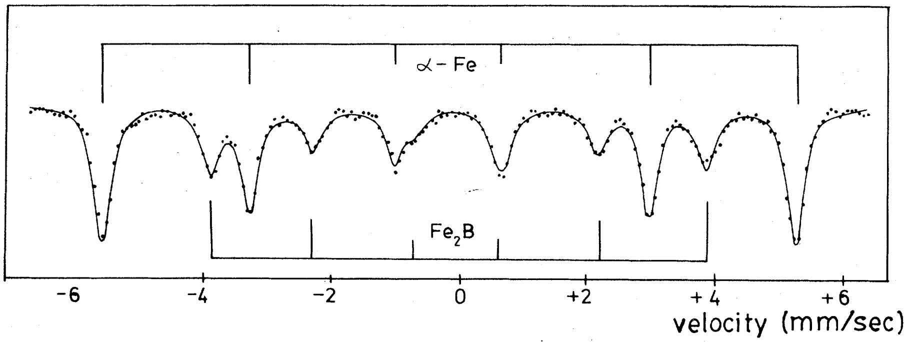

FIG. 13. Mössbauer spectrum of the $Fe_{85}B_{15}$ (CRIP) alloy, heat treated to the two-phase, stable crystalline state.

surements. Mössbauer spectroscopy also detects only the equilibrium phases, α-Fe and Fe_2B in a 15-at.%-B sample, heat treated at 1000 K for 1 h (see Fig. 13). The heat effect of the $Fe_3B \rightarrow \alpha$-Fe + Fe_2B transformation is too small to be resolved by the DSC. Traces of the Fe_2B phase can also be detected in the Mössbauer spectrum of samples heat treated to the end of the second crystallization stage. It means that while Fe_3B transforms to the stable phases, the DSC curve goes back to the baseline (see Fig. 8) indicating the end of the crystallization process. This result can be interpreted by supposing that (a) the enthalpy change of the transformation is very small and (b) the transformation rate is not significant, i.e., the transition is sluggish.

The easiest interpretation of the single state transformation observed in the $16 < c_B < 25$ at.% concentration region is that of the eutectic (α-Fe + Fe_3B) crystallization.[78(d)] This kind of mechanism has been also postulated for the Fe-P-C system.[79] The investigation of transformation kinetics cannot disprove this mechanism in the Fe-B system. The respective thermal activation energies of the distinct stages ($12.5 < c_B < 16$ at.%), determined by the peak-shift method,[38] are quite different from each other (see Table I). A detailed kinetic investigation on the 17- and 20-at.%-B samples reveals that the transformation can be described with a single activation energy, from $C = 10\%$ crystallized fraction to $C = 90\%$ (see Sec. II A).

The shape of the transformation rate curves of the 17- and 20-at.%-B samples are quite different. The markedly asymmetric shape of the crystallization curve for the 17-at.% alloy (see Fig. 14) and the Avrami exponents, n, (see Table I) determined from the transformation rate, indicate some kind of other processes, which are not explained by the hypothesis of the eutectoid crystallization. The n values for the 17-at.%-B sample are markedly dependent on the heating rate. Similar results for other systems have been frequently reported on the basis of isothermal measurements. Other investigators have also found that kinetic exponent depends on temperature.[35–40]

The normalized α-Fe fraction in partly crystalline 17-at.%-B alloys (determined from Mössbauer spectroscopy) is plotted in Fig. 15 against the total crystalline fraction measured by the DSC. The amount of α-Fe increases fast at the beginning and then saturates at approximately 70% crystalline fraction. It means that α-Fe crystallizes first in this case too, i.e., the seemingly single stage transformation has a fine structure quite similar to the distinct processes.

The crystallization of Fe-B glasses follows the same sequence in the whole $12.5 < c_B < 25$ at.% concentration range. The apparent thermal activation energies, determined from the Arrhenius-type rate factor, can describe the processes in only a relatively narrow temperature range. The crystallization of both α-Fe and Fe_3B can be characterized by a single activation energy when the transformations proceed in nearly the same temperature range. The great difference between the activation energies of the distinct stages measures the temperature dependence of the apparent activation energy. A similar behavior, i.e., a different activation energy for the distinct stages of crystallization has been reported by Boswell.[80] As the apparent activation energy increases with temperature, the dependence cannot be derived from a simple Fulcher-type equation as it has been reported by Chen.[81]

The concentration dependence of crystallization temperature and enthalpy change can be seen in Figs. 10 and 16. No trace of extra stabilization can be detected at the eutectic point (17-at.% B). It is in good accordance with the concepts of Chen,[82] who has pointed out that the enhanced glass-forming ability is rather connected to the destabilization of crystalline mixture than to the extra stability of the noncrystalline phase.

The decrease of enthalpy change with increasing B concentration is remarkable. Only a part of the decrease can be accounted for by the diminishing magnetic energy.[83] The decrease of the excess energy of the glassy state as one approaches the composition where the Fe to B ratio is 3 : 1, also favors the interpretation that the glassy structure should be based on a locally distorted Fe_3B quasicrystalline unit.

IV. CONCLUSIONS

The main results of our work can be summarized with the following conclusions:

TABLE I. Kinetic parameters.

Compositon c_B (at.%)	E_a^1 (eV atom^{-1})	E_a^2 (eV atom^{-1})	k_0 (sec^{-1})	n
15 (CRIP)	2.2 ± 0.2	3.2 ± 0.2		
17 (CRIP)		2.75 ± 0.05	$3 \pm 1) \times 10^{17}$	3–6
20 (MG 2605)		2.5 ± 0.05	$(1.2 \pm 1) \times 10^{16}$	2.2 ± 0.2

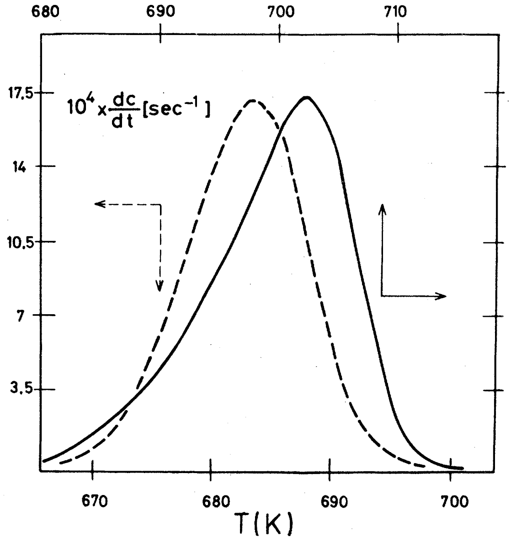

FIG. 14. Comparison of the crystallization rate in $Fe_{80}B_{20}$ (MG 2605) (dashed line) and in $Fe_{83}B_{17}$ (CRIP) (continuous line).

(i) The concentration dependence of the iron hyperfine field and iron average magnetization does not support the donor model. These quantities are approximately proportional to each other as in intermetallic compounds suggesting a rather localized type of behavior.

(ii) The hyperfine-field distribution of metallic glasses cannot be explained using the DRPHS approximation. A quasicrystalline model, based on the metastable Fe_3B intermetallic compound satisfactorily describes the main experimental observations.

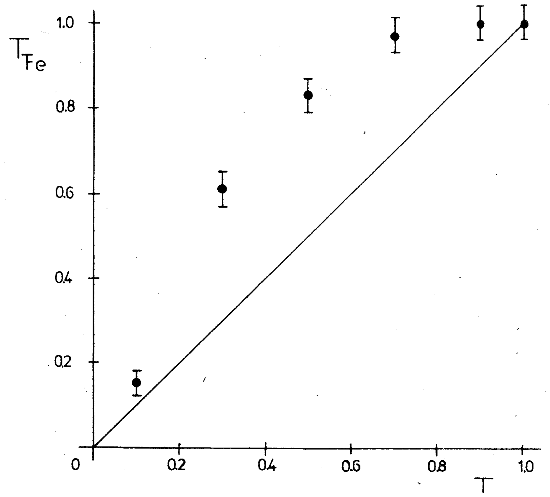

FIG. 15. Relative α-Fe fraction T_{Fe} vs total crystalline fraction T for $Fe_{83}B_{17}$ (CRIP) partly crystalline alloys.

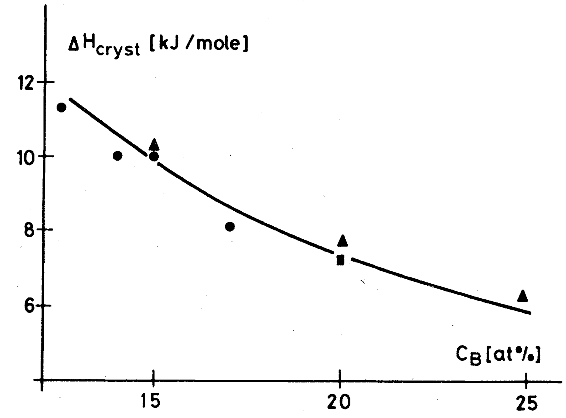

FIG. 16. Concentration dependence of change in heat content due to crystallization. Same symbols as in Fig. 7.

(iii) Static magnetic measurements indicate significant thermal relaxation in the glassy state. The Curie point of Fe-B metallic glasses increases with increasing B concentration.

(iv) The crystallization sequence in the whole $12 < c_B < 25$ at.% concentration range can be described as

$$a\text{-}Fe_{100-c_B}B_{c_B} \rightarrow a\text{-}Fe_{75}B_{25} + \alpha\text{-}Fe\,,$$

$$a\text{-}Fe_{75}B_{25} \rightarrow Fe_3B\,,$$

$$Fe_3B \rightarrow Fe_2B + \alpha\text{-}Fe\,.$$

We have not detected any traces of the Fe_4B compound, predicted by Köster and Herold,[84] neither the $Fe_{23}B_6$ nor the orthorhombic Fe_3B compounds which were suggested by Franke et al.[78(b)]

(v) The structure of Fe_3B metastable intermetallic compound which forms as the crystallization product in the Fe-B glasses is significantly different from cementite. It can be described by Fe_3P-type tetragonal structure,[78] in good agreement with the results of Wäppling et al.,[85] namely, that P can be substituted by B up to the concentration $Fe_3B_{0.9}P_{0.1}$ without any change in the Fe_3P crystal structure.

(vi) The temperature dependence of the apparent energy of thermal activation cannot be determined from a simple Fulcher-type equation. The dependence of the Johnson-Mehl-Avrami exponent, n, on external parameters is a consequence of the overlap between two processes. It prevents any simple interpretation in terms of the dimentionalities of growth or diffusion and time dependence of nucleation.[86]

(vii) No extra stability can be detected either at the eutectic point or at 20-at.% B. The decreasing heat of crystallization towards the Fe to B 3 : 1 composition is in agreement with the Fe_3B-based quasicrystalline concept.

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