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### High-pressure Mössbauer studies of amorphous and crystalline $\text{Fe}_3\text{B}$ and $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$

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The pressure dependence of the  $^{57}\text{Fe}$  hyperfine parameters in amorphous and crystalline  $(\text{Fe}_{1-x}\text{Ni}_x)_3\text{B}$  alloys ( $x=0$  and  $0.75$ ) were measured by Mössbauer spectroscopy. A similar response of *all* hyperfine parameters for both the amorphous and crystalline phases with decreasing volume was observed. The pressure dependence of the hyperfine field indicates that the distribution of Fe-B interatomic distances is about two times narrower than that of the Fe-Fe interatomic distances measured by x-ray scattering.

#### I. INTRODUCTION

The determination of the local structure of amorphous metals or alloys is fundamental in understanding the specific properties of these materials. Direct information on the atomic arrangement is obtained from x-ray and neutron scattering measurements in terms of the radial distribution function (RDF). The RDF provides the *average* interatomic distances and coordination numbers—but no detailed information on the probability distribution of the different possible atomic configurations is obtained. Also, three independent scattering measurements are necessary to characterize a binary alloy which are not available in most cases.

Indirect information on the very local surroundings can be obtained via NMR or Mössbauer (ME) measurements. The hyperfine interactions (hyperfine field, quadrupole splitting, isomer shift) depend sensitively on the nearest-neighbor configuration of the nuclei investigated. The hyperfine field (and isomer shift) is determined mostly by the number and the distance of the surrounding atoms. They are less dependent on the geometrical arrangement of the neighbors which influences strongly the value of the quadrupole interaction.  $^{57}\text{Fe}$  ME experiments on ferromagnetic transition-

metal—metalloid glasses show the presence of broad lines which correspond to the distribution of the hyperfine fields,  $p(B)$ . It has been explained<sup>1</sup> that in intermetallic compounds the iron hyperfine field  $B$  is proportional to the iron magnetic moment which is determined mainly by the number of nearest metalloid neighbors. In amorphous systems  $p(B)$  corresponds not only to the fluctuation in the nearest-metalloid-neighbor number but the fluctuation in the iron-metalloid distances results in a comparable additional broadening of the individual distributions determined by the number of metalloid neighbors.

The nearest-neighbor peak (i.e., transition-metal—metalloid peak) of the radial distribution function also describes fluctuation in both interatomic distances and environments (coordination numbers). The width of the hyperfine field distribution is obviously related to the width of this nearest-neighbor peak via the distance dependence of the hyperfine field. Pressure dependent Mössbauer measurements are very important in establishing the connection between these different kinds of experimental information. To simplify the following analysis it will be assumed that the fluctuation in the number of nearest-metalloid-neighbors contributes about the same extent both to  $p(B)$  and to the transition-metal—metalloid peak of the RDF, that is, we will concentrate on

the effect of structural (or topological) disorder. On the basis of crystalline  $\text{Fe}_3\text{B}$  data<sup>2,3</sup> about half of the widths can be attributed to the contribution of chemical disorder. In general, it is difficult to separate the transition-metal—metalloid peak of the RDF from the much more dominant transition-metal—transition-metal peak when x-ray scattering was used for the determination of the RDF.

In this paper we present the first results of high-pressure  $^{57}\text{Fe}$  Mössbauer experiments performed at 300 and 340 K, respectively, on amorphous and crystalline  $(\text{Fe}_{1-x}\text{Ni}_x)_3\text{B}$  alloys. Two compositions,  $x=0$  and 0.75, were selected because of the following reasons. Both alloys crystallize into a single phase having the tetragonal  $\text{Ni}_3\text{P}$  and the orthorhombic  $\text{Ni}_3\text{B}$  structure, respectively.<sup>2</sup> Amorphous  $\text{Fe}_3\text{B}$  can be studied in the magnetically ordered state only (its Curie temperature  $T_c \approx 725$  K is above its crystallization temperature  $T_{\text{cryst}} \approx 700$  K. Information about the volume dependence of the magnetic hyperfine field  $B$  at the  $^{57}\text{Fe}$  nucleus can be gained in both phases.  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  has its  $T_c = 270$  K well below  $T_{\text{cryst}} \approx 700$  K, i.e., the paramagnetic as well as the ferromagnetic state is accessible for ME measurements. In the paramagnetic phase the volume dependence of the quadrupole interaction and the isomer shift can be easily studied in the amorphous and crystalline phase.

This system offers another interesting feature: The crystalline phase has its  $T_c$  at 320 K. Thus a high-pressure ME experiment on amorphous  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  at 300 K is sensitive for the detection of a possible partial, pressure-induced crystallization (i.e., a magnetically split hyperfine pattern should appear in addition to the quadrupole doublet of the paramagnetic, amorphous phase).

The selection of these systems was motivated also by the observation that the chemical and topological short-range order of these glasses as inferred from the concentration dependence of the hyperfine field and quadrupole splitting is rather near to that of the crystalline counterparts.<sup>2</sup> It should be mentioned that Liu *et al.*<sup>4</sup> recently reported high-pressure ME absorption experiments on the ferromagnetic Metglass 2826A ( $\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$ ) alloy. Their results indicate a decrease of  $B$  and  $T_c$  with pressure. However, it is difficult to interpret their data due to the complex composition of the sample and its complicated magnetic structure (coexistence of ferromagnetic and paramagnetic environments).

## II. EXPERIMENTAL DETAILS

The metallic glasses used in this work were ribbons (width  $\approx 0.5$ –2 mm, thickness  $\approx 20$   $\mu\text{m}$ ) prepared by the melt-spinning technique at the Central Research Institute for Physics, Budapest by A. Lovas.

The ribbons were mounted together and cut to give a disk of  $\approx 4$ -mm diameter suitable for the high-pressure cell. The high-pressure ME absorption experiments were performed in a Chester-Jones-type high-pressure setup with  $\text{B}_4\text{C}$  anvils as described elsewhere.<sup>5</sup> The high-pressure cell is based on a pyrophyllite ring supported from outside by a steel belt which provides a quasihydrostatic pressure up to about 70 kbar. The pressure calibration at 300 K was performed with the help of a lead manometer and the pressure calibration of the lead resistivity as given by Eiling *et al.*<sup>6</sup>

The crystalline phases  $\text{Fe}_3\text{B}$  and  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  have been obtained by crystallization of the corresponding metallic glasses [ $\text{Fe}_3\text{B}$ :  $\approx 20$  min at 750 K,  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ :  $\approx 1.5$  h at 690 K]. Thus we have used the *same* sample for the comparison between the amorphous and crystalline state.

There is a basic problem in high-pressure ME absorption experiments on  $^{57}\text{Fe}$  samples using  $\text{B}_4\text{C}$  anvils:  $\text{B}_4\text{C}$  contains  $^{57}\text{Fe}$  impurities which cannot be removed without destroying the mechanical properties of this material. These impurities result in a fairly complicated ME spectrum which will be superimposed on the ME spectrum of the sample studied. For this reason each measurement was made twice: with the sample [spectrum (a)] and without the sample [spectrum (b)]. All spectra shown have been obtained by subtraction of spectrum (b).

The experimental setup used by Liu *et al.*<sup>4</sup> is essentially the same described by Debrunner *et al.*<sup>7</sup> and does not have the problem with the  $\text{B}_4\text{C}$  anvils. However, it has the disadvantage that the absorber size is limited to  $\approx 0.5$ -mm diameter and the solid angle is poor.

The ME absorption spectra were taken with a sinusoidally moved  $^{57}\text{Co:Rh}$  source. Both source and absorber were kept at 300 and 340 K during the ME runs.

## III. RESULTS

The pressure dependence of the hyperfine field was measured in the amorphous and crystalline  $\text{Fe}_3\text{B}$  samples at 300 K. The quadrupole interaction cannot be studied in this magnetically ordered

state because it is averaged out due to the distribution of the angle between the direction of the electric field gradient and that of the magnetic moment. In the paramagnetic state there is no such difficulty and the pressure dependence of the quadrupole splitting  $\Delta E_Q$ , was measured in the  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  alloys. The change of the isomer shift  $S$  under pressure was studied in both sets of samples. The results are as follows.

(a)  $\text{Fe}_3\text{B}$ . The ME absorption spectra of amorphous  $\text{Fe}_3\text{B}$  at 300 K ( $T_c = 725$  K) and pressures  $p = 0, 60$  kbar and after pressure release are given in Figs. 1(a)–1(c), respectively. The spectra of the amorphous sample were fitted with a magnetically split six-line pattern assuming a Gaussian distribution of the hyperfine field,  $B$  ( $p(B) \propto \exp\{-\frac{1}{2} \times [(B - \bar{B}) / \Delta B]^2\}$ );  $\bar{B}$  is the mean value of the hyperfine field distribution,  $\Delta B$  is the standard deviation of the Gaussian distribution. The spectra of the crystalline sample were described with three six-line patterns corresponding to the three inequivalent Fe sites in  $\text{Fe}_3\text{B}$ .<sup>3</sup> The relative line intensities within the six-line patterns deviate from the values 3:2:1:1:2:3 characteristic of random spin distribution due to well-known texture effects in the preparation of metallic glass ribbons. For high

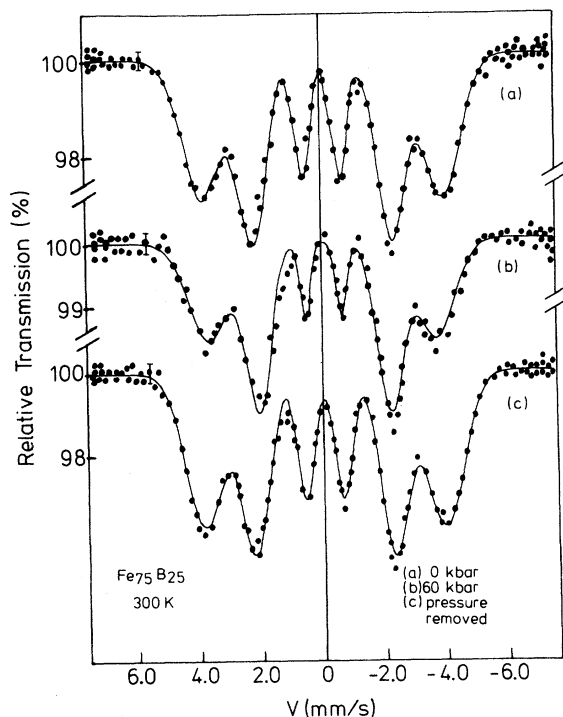


FIG. 1. Mössbauer spectra of amorphous  $\text{Fe}_3\text{B}$  at  $T = 300$  K without applied pressure (a), with 60 kbar applied pressure (b), and after pressure release (c).

pressure the spin direction is tilted more in the ribbon plan, i.e., off from the  $\gamma$ -ray direction. Thus the intensity of lines 2 and 5 were treated as a free parameter in our fitting procedure. Table I gives the  $\bar{B}$  and  $\Delta B$  values obtained from least-squares fits to the measured spectra. The difference in the  $\bar{B}$  values of the amorphous and crystalline phases is due to the fact that our measurements have been performed at 300 K: The amorphous  $\text{Fe}_3\text{B}$  has a lower  $T_c$  than the crystalline  $\text{Fe}_3\text{B}$  and its  $\bar{B}(T)$  curve lies below that of the crystalline curve. At  $T = 5$  K both  $\bar{B}$  values are the same [ $\bar{B}(5 \text{ K}) = 27.3 \pm 0.4 \text{ T}$ ].<sup>2</sup> The value of  $\bar{B}$  for the amorphous sample is reversible by removing the pressure (see Table I).

No pressure-induced changes in the isomer shift  $S$  could be observed ( $\partial S / \partial P \lesssim 5 \times 10^{-4} \text{ mm/s kbar}^{-1}$ ) within the experimental error which is larger in the case of these complex ferromagnetic spectra than in the case of simple paramagnetic spectra.

(b)  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ . The ME absorption spectra of amorphous  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  at 300 K ( $T_c = 274$  K) and at pressures  $p = 0, 60$  kbar and after pressure release are shown in Figs. 2(a)–2(c), respectively. The corresponding spectra of the crystalline phase  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  were obtained at 340 K ( $T_c = 334$  K). All spectra have been fitted with two Lorentzian lines corresponding to a quadrupole doublet. The data obtained from least-squares fits are given in Table II. The reversibility of both the isomer shift and the quadrupole splitting after removing the applied pressure can also be seen from the data in Table II.

The pressure dependence of the isomer shift ( $\partial S / \partial p$ ), given in Table II, has not been corrected for changes in the second-order Doppler shift (SOD). For  $^{57}\text{Fe}$  ( $\partial S_{\text{SOD}} / \partial \ln V$ )<sub>T</sub> is more than 1 order of magnitude smaller than ( $\partial S / \partial \ln V$ ) and therefore can be neglected.<sup>8</sup>

No pressure-induced crystallization is observed for amorphous  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  at  $p = 60$  kbar and  $T = 300$  K.

#### IV. DISCUSSION

The pressure dependence of the Mössbauer parameters  $\partial X / \partial p$  ( $X$  is the isomer shift, quadrupole splitting, hyperfine field) should be transformed into the physically more relevant ( $\partial X / \partial \ln V$ ) values. For this transformation the value of the compressibility  $\kappa = -(\partial \ln V / \partial p)$  of

TABLE I. Pressure dependence of the Mössbauer parameters of amorphous and crystalline  $\text{Fe}_3\text{B}$  at  $T=300$  K.  $\bar{B}$  is the average hyperfine field,  $\Delta B$  is the standard deviation of the hyperfine field distribution.

	$T$ (K)	$P$ (kbar)	$\bar{B}$ (T)	$\Delta B$ (T)	$\Delta B/\bar{B}$ (%)	$\partial \ln \bar{B} / \partial p$ (kbar $^{-1}$ )	
$\text{Fe}_3\text{B}$ amorphous	300	0	24.4(1)	3.6(2)	15.1(8)		
	300	60	23.0(1)	4.2(2)	17.6(8)	$-0.89(10) \times 10^{-3}$	
	300	0 <sup>a</sup>	24.5(1)	3.5(2)	14.3(8)		
			$B_1$ (T)	$B_2$ (T)	$B_3$ (T)	$\bar{B}^b$ (T)	
$\text{Fe}_3\text{B}$ crystalline	300	0	30.0(1)	27.7(1)	23.4(1)	27.0(1)	$-0.92(10) \times 10^{-3}$
	300	60	28.3(1)	26.2(1)	21.9(1)	25.5(1)	

<sup>a</sup>After removing the pressure.

<sup>b</sup> $\bar{B} = \frac{1}{3}(B_1 + B_2 + B_3)$ .

these compounds should be known. No direct  $\kappa$  data are available on the investigated alloys, however a value of  $\kappa = 6 \times 10^{-4}$  kbar $^{-1}$  can be extrapolated from the measured  $\kappa$  values of different Fe and Ni containing metallic glasses.<sup>9</sup> This value of  $\kappa$  will be used in all later transformations assuming that it is identical in amorphous and crystalline states and independent of composition. This assumption may introduce an estimated 10% sys-

tematical error in the further calculated values but it is not significant regarding the qualitative results.

#### A. Isomer shift

Both the amorphous and the crystalline phase of  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  have isomer shift values which are more positive than that of the Fe metal. This means that the electron density  $\rho(0)$  at the  $^{57}\text{Fe}$  nucleus is lower.

This decrease in  $\rho(0)$  can be explained by assuming that the metalloid (B) neighbors cause a rearrangement in the charge distribution of iron increasing its  $d$  character and decreasing its  $s$  character. The isomer shift decreases, i.e.,  $\rho(0)$  increases, in both phases with increasing pressure. The values of  $\partial S/\partial p$  (see Table II) are the same for the amorphous and crystalline phase within the experimental errors. Using the above mentioned value of  $\kappa$  gives  $\partial S/\partial \ln V \simeq 0.6$  mm/s for both the amorphous and the crystalline system.

#### B. Quadrupole interaction

No measurable pressure dependence of the quadrupole interaction was observed in the amorphous and crystalline  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ , i.e.,  $\partial \Delta E_Q / \partial p \lesssim 1 \times 10^{-4}$  mm/s kbar $^{-1}$  or  $\partial \Delta E_Q / \partial \ln V \lesssim 0.16$  mm/s. On the other hand, the quadrupole splitting of the amorphous and crystalline alloys differs by  $\sim 0.12$  mm/s (Table II, Ref. 2). The observed pressure independence of  $\Delta E_Q$  rules out the possibility that this difference is caused by the larger Fe-B bond length of the amorphous state. Name-

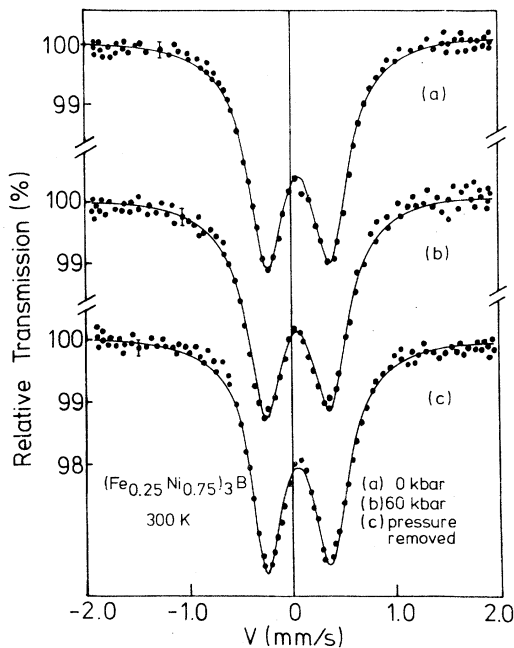


FIG. 2. Mössbauer spectra of amorphous  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  at 300 K without applied pressure (a), with 60 kbar applied pressure (b), and after pressure release (c).

TABLE II. Pressure dependence of the Mössbauer parameters of amorphous and crystalline  $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$  at  $T=300$  and  $340$  K, respectively.  $S$  is the isomer shift,  $\Delta E_Q$  is the quadrupole splitting.

	$T$ (K)	$P$ (kbar)	$S^a$ (mm/s)	$\Delta E_Q$ (mm/s)	$\partial S/\partial p$ (mm/s) kbar $^{-1}$	$\partial \Delta E_Q/\partial p$ (mm/s) kbar $^{-1}$
$(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ amorphous	300	0	0.175(6)	0.636(6)		
	300	60	0.158(6)	0.640(6)	$2.8(15) \times 10^{-4}$	$\leq 10^{-4}$
	300	0 <sup>b</sup>	0.178(6)	0.638(6)		
$(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ crystalline	340	0	0.157(4)	0.751(4)		
	340	60	0.131(4)	0.744(4)	$4.5(10) \times 10^{-4}$	$\leq 10^{-4}$

<sup>a</sup>Center shift relative to Fe metal at 300 K.

<sup>b</sup>After removing the pressure.

ly, the density of amorphous alloys is smaller by about 1–2 % than that of the crystalline alloys with the same composition. This difference would result in only about  $(0.16-0.32) \times 10^{-2}$  mm/s difference on the  $\Delta E_Q$  values (in this estimation the above obtained value of  $\partial \Delta E_Q/\partial \ln V$  was used) which is orders of magnitude smaller than the observed one. Since the difference in the quadrupole interaction of amorphous and crystalline alloys is not caused by the differences in interatomic distances the most probable reason for the difference remains the distortion of the Fe–B bond angles as in amorphous semiconductors<sup>2</sup> but some effect of possibly different second- and further neighbor configurations of the Fe atom cannot be excluded.

### C. Magnetic hyperfine interactions

The pressure dependence of the magnetic hyperfine field at the  $^{57}\text{Fe}$  nucleus in  $\text{Fe}_3\text{B}$  is about the same for both amorphous and crystalline state  $\partial \ln \bar{B}/\partial p = -(0.9 \pm 0.1) \times 10^{-3}$  kbar $^{-1}$ . There is a difference in the mean values between amorphous and crystalline  $\text{Fe}_3\text{B}$  because the high-pressure experiments were performed at 300 K and the Curie temperature of the amorphous and crystalline states are different by about 50 K.<sup>2</sup> The  $T_c$  of amorphous  $\text{Fe}_3\text{B}$  is the lower one. Therefore, one has to take into account the affect of the pressure on  $T_c$  for a careful analysis. Assuming that a pressure of 60 kbar will reduce  $T_c$  by approximately 30 K and using a typical reduced magnetization curve we can estimate a decrease of  $\leq 0.14$  T of  $\bar{B}$  at 300 K resulting from this supposed decrease of  $T_c$  with pressure, a value which is an order of magnitude smaller than the observed decrease in  $\bar{B}$

for the applied pressure.

Using the above mentioned value of compressibility  $\kappa = 6 \times 10^{-4}$  kbar $^{-1}$  we obtain  $\partial \ln \bar{B}/\partial \ln V = 1.5$  for both the amorphous and crystalline state of  $\text{Fe}_3\text{B}$ . This value is much higher than that of  $\alpha\text{-Fe}$  [ $(\partial \ln \bar{B}/\partial \ln V) = 0.372 \pm 0.026$ ].<sup>10</sup> The high-pressure Mössbauer experiments of Liu *et al.*<sup>4</sup> give an even larger value of  $\partial \ln \bar{B}/\partial p = -3 \times 10^{-3}$  kbar $^{-1}$  for the Metglass 2826A ( $\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$ ) alloy. These high values of  $\partial \ln \bar{B}/\partial \ln V$  indicate the importance of Fe–B bonds in these systems and the similar values of the amorphous and crystalline state suggest similar Fe–B bonding in these alloys.

These findings are quite different from the results of high-pressure ( $p \leq 4$  kbar) magnetization measurements on some nonstoichiometric amorphous alloys<sup>11</sup>: a decrease in the saturation magnetization  $\sigma_0$  of  $\partial \ln \sigma_0/\partial p \simeq -5 \times 10^{-3}$  kbar $^{-1}$  was found for the amorphous state, while an increase of  $\partial \ln \sigma_0/\partial p \simeq +10 \times 10^{-3}$  kbar $^{-1}$  for the crystallized samples. Since these are nonstoichiometric systems and the crystalline samples consist of mixtures of different crystalline phases, the different behavior of the amorphous and crystalline samples is not informative about the effect of structural disorder on the pressure dependence of the magnetization.

### D. Relation between atomic structure and hyperfine field

The atomic structure of amorphous alloys is characterized by radial distribution function obtained via scattering measurements. In transition-metal (TM)–metalloid (M) systems the x-ray scattering measurements provide mostly the TM–TM distribution because of the too weak scattering

of the metalloid atoms. It has been found that the first peak of the RDF can be well described<sup>7,12</sup> by a Gaussian form,

$$p(r) \propto \exp \left[ -\frac{1}{2} \left( \frac{r - r_{\text{Fe-Fe}}}{\Delta r_{\text{Fe}}} \right)^2 \right]$$

which corresponds to a  $\Delta r_{\text{Fe}}$  fluctuation around some average value,  $r_{\text{Fe-Fe}}$  in interatomic distances representing the structural disorder. Typical values of the relative standard deviation  $\Delta r_{\text{Fe}}/r_{\text{Fe-Fe}}$  are about 7.5% as measured<sup>3</sup> by x-ray scattering in amorphous  $\text{Fe}_{80}\text{B}_{20}$  and it is quite insensitive for changes in components or in concentrations.

On the other hand, Mössbauer experiments give information on the distribution of the metalloid atoms around Fe. The measured hyperfine field distribution  $p(B)$  can be also well described with a Gaussian form ( $p(B) \propto \exp\{-\frac{1}{2}(B-\bar{B})/[\Delta B]^2\}$ ), where the standard deviation  $\Delta B$  is determined mostly by the fluctuation in the Fe-B overlap. The typical value of  $\Delta B/\bar{B}$  in Fe-B metallic glasses is about 15% (Table I). This fluctuation in the iron hyperfine field can be used to estimate the fluctuation of the Fe-B interatomic distances,  $\Delta r_{\text{B}}$  when the pressure dependence of the iron hyperfine field is known, as follows:

$$\Delta B = \left( \frac{\partial \bar{B}}{\partial r} \right) \Delta r_{\text{B}},$$

i.e.,

$$\frac{\Delta r_{\text{B}}}{r_{\text{Fe-B}}} = \frac{1}{3(\partial \ln \bar{B} / \partial \ln V)} \left( \frac{\Delta B}{\bar{B}} \right).$$

Using the values given in Table I we obtain  $\Delta r_{\text{B}}/r_{\text{Fe-B}} \approx 3.4\%$  for the relative fluctuation in the iron-boron distances. This value is substantially lower than the above mentioned relative scattering of 7.5% of Fe-Fe distances. It is in good agreement, however, with the results of extended x-ray absorption fine structure measurements<sup>13</sup> on amorphous  $\text{Pd}_3\text{Ge}$  where smaller than 4% relative fluctuation was found in the TM-M interatomic distances.

## V. CONCLUSION

High-pressure Mössbauer experiments on amorphous and crystalline alloys are very informative about the local atomic structure of these materials. The similar response of *all* hyperfine parameters observed for both the amorphous and crystalline

alloys with decreasing volume supports the earlier results<sup>2,3</sup> according to which the assumption of similar amorphous and crystalline local structure is a good approximation in this  $(\text{Fe}_{1-x}\text{Ni}_x)_3\text{B}$  system.

The pressure (i.e., volume) dependence of the hyperfine parameters is necessary to convert these quantities into more direct structural data, like fluctuation in transition-metal—metalloid distances. This conversion is essentially model independent, the only important assumption is the assumption of a homogeneous, isotropic effect of pressure on interatomic distances and hyperfine parameters.

In the present paper we have performed such conversion in a stoichiometric metallic glass which has resulted in much smaller relative scattering of transition-metal—metalloid distances (3.4%) than the relative scattering in the metal-metal distances (7.5%) measured by x-ray scattering. This result suggests strong similarities between the atomic structure of metallic glasses and covalent glasses. Generally, in the radial distribution function of covalent glasses the peak corresponding to the nearest neighbors is quite sharp and the substantially larger fluctuation in second- or further neighbor distances originates from the fluctuation in the bonding angles. The present results indicate similar structural models for metallic glasses: the position (both distances,  $r_{\text{Fe-B}}$  and the B—Fe—B bonding angles) of the metalloid atoms relative to the transition-metal atom is quite well determined, as the pressure dependence of the hyperfine field and quadrupole splitting shows. This amorphous structural unit (cluster) is quite near to the similar unit of crystalline compounds<sup>14</sup> but slightly distorted as the difference between the amorphous and crystalline  $\Delta E_Q$  indicates. The more than twice larger fluctuation in Fe-Fe than in Fe-B distances corresponds to a scattering of  $\approx 6^\circ$  in the Fe—B—Fe bonding angles with respect of the crystalline values. Apparently, the main difference between the structural units of covalent glasses and metallic glasses is only the size of the cluster: In covalent glasses the coordination is  $\leq 4-5$  while in metallic glasses it is around 9.

*Note added in proof.* According to a recent high-resolution ( $Q_{\text{max}} = 25.8 \text{ \AA}^{-1}$ ) time-of-flight neutron diffraction study of amorphous  $\text{Fe}_{81}\text{B}_{19}$  by E. Sváb, S. N. Ishmaev, F. Forgács, I. P. Sadikov, and A. A. Chezyshav [International Conference on Amorphous Systems Investigated by Nuclear Methods, Balatonfüred, Hungary, 1981, Nucl. Instrum. Methods (in press)], the upper limit for the

full halfwidth of the Fe-B nearest-neighbor peak in the reduced radial distribution function is about 0.3 Å. This value is much smaller than that of the Fe-Fe nearest-neighbor peak, which was found to be 0.44 Å. Since the corresponding value of the Fe-B distance fluctuation deduced from the present Mössbauer data is  $0.20 \pm 0.04$  Å, the agreement is remarkably good.

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