

$(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$: A model system to study the local structure in metal-metalloid glasses by means of Mössbauer spectroscopy

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High-pressure Mössbauer studies of amorphous and crystalline $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ at 4.2 K are presented. The similar response of *all* hyperfine parameters for both the amorphous and crystalline phase with decreasing volume indicates similar local structure in the two phases. The analysis of the pressure dependence of the hyperfine field B_{eff} at the ^{57}Fe nucleus shows, that (i) the magnitude of B_{eff} in this metal-metalloid glass is mainly determined by the iron-boron (Fe-B) interaction and (ii) the fluctuation in the Fe-B distances is only about 3% compared with about 7.8% in the Fe-Fe distances. The Mössbauer spectrum of the amorphous system in the paramagnetic phase (Curie temperature $T_C = 276$ K) with an external magnetic field of 5 T gives evidence for the occurrence of large spin clusters at 300 K. The pressure dependence of T_C for both phases has been measured with the "thermal scanning" technique and is discussed within the framework of existing theoretical approaches.

I. INTRODUCTION

The determination of the local structure in metallic glasses is of major interest for the understanding of these metastable, amorphous systems. Metal-metalloid glasses are one special class of metallic glasses. Fe-containing metal-metalloid glasses have been widely used for ^{57}Fe Mössbauer-effect (ME) studies with the hope that ME spectroscopy, as a microscopic tool of measurement, may give some information on the local structure in these systems. However, quite opposing models have been proposed for the interpretation and evaluation of the ME spectra in metal-metalloid glasses.^{1,2} Thus the former optimistic point of view of ME spectroscopists has by now turned over to a rather pessimistic one, stating that "almost any assumed model can be correlated with or derived from the broad hyperfine spectra of these materials."³ From this it is quite clear that additional external parameters are necessary if one wants to derive some model independent conclusion on the atomic arrangement in these systems by means of ME spectroscopy. Such additional parameters are, for example, external pressure or an applied magnetic field.

It has been shown in our previous paper⁴ that the pressure dependence of the hyperfine (hf) parameters measured in a high-pressure ME experiment allows one to derive some conclusions on the local structure which are rather model independent. The analysis of these data, for example, leads us to the conclusion that the relative variation of the Fe-B distances $r_{\text{Fe-B}}$ in $\text{Fe}_{75}\text{B}_{25}$ is almost a factor of 2 smaller than the relative variation in the Fe-Fe distances $r_{\text{Fe-Fe}}$, i.e., $\Delta r_{\text{Fe-B}}/r_{\text{Fe-B}} \simeq 0.5 \Delta r_{\text{Fe-Fe}}/r_{\text{Fe-Fe}}$. This result has been verified by quite costly and large-scale

scattering experiments recently reported by Lamparter *et al.*⁵; three independent scattering experiments on isotopically substituted $\text{Fe}_{80}\text{B}_{20}$ had to be performed. The results showed the much stronger correlation in the Fe-B distances, compared to that in the Fe-Fe distances, thus confirming our indirect results from high-pressure ME spectroscopy on $\text{Fe}_{75}\text{B}_{25}$.

In this paper we present extensive ME studies of the metal-metalloid glass $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ using the high-pressure technique and applying an external magnetic field in the paramagnetic state. After introducing the $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ system we inspect the ME spectrum of a paramagnetic metallic glass in an external field with the possible information concerning the local geometry. The experimental results will be discussed in detail in connection with the local structure of this metal-metalloid glass.

II. THE METAL-METALLOID GLASS

$(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$

We believe that the metal-metalloid glass $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ is an ideal model system to study the local structure in the class of metal-metalloid glasses for the following reasons.

(i) It is a ferromagnetic glass with its Curie temperature $T_C = 276$ K well below the so-called crystallization temperature $T_{\text{crys}} \simeq 700$ K. Thus $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ can be studied in the paramagnetic as well as in the magnetically ordered state. This allows the measurement of all three hf parameters: isomer shift S , electrical quadrupole splitting ΔE_Q , and magnetic hf splitting due to the effective magnetic hf field B_{eff} at the ^{57}Fe nucleus.

(ii) It is a stoichiometric metallic glass, i.e., there is a crystalline counterpart $[\text{Fe}_{0.25}\text{Ni}_{0.75}]_3\text{B}$ with the orthorhombic Ni_3B structure⁶ whose hf parameters x_i and pressure derivatives $\partial x_i/\partial p$ can be compared with their corresponding values in the glassy state.

Up to now $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ has been studied by ME at various temperatures and ambient pressure by Balogh *et al.*⁷ The first high-pressure ME experiments on paramagnetic $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ at $T=300$ K have been published recently.⁴

III. ME SPECTRA OF A PARAMAGNETIC METALLIC GLASS WITH EXTERNAL MAGNETIC FIELD

⁵⁷Fe ME spectra of a system in the paramagnetic phase show a quadrupole doublet, whose splitting ΔE_Q gives information on the magnitude of $V_{zz}(1+\eta/3)^{1/2}$ [V_{zz} is the mean component of the electric field gradient (EFG) tensor, η is the so-called asymmetry parameter $\eta=(V_{xx}-V_{yy})/V_{zz}$]. No information is obtained about the *sign* of V_{zz} or the magnitude of η . The sign of V_{zz} is revealed if both the electric quadrupole and magnetic dipole interaction are present. In the case of magnetically ordered amorphous systems, however, the random distribution of the principal axis of the EFG tensor with respect to the magnetization direction averages out the effective quadrupole interaction and results in a nearly zero apparent quadrupole interaction in the broad ⁵⁷Fe hf spectra of magnetically ordered metallic glasses. Thus, important information is lost which can be useful in the determination of the local structure in amorphous systems. The Bernal model (random atomic arrangement), for example, predicts the occurrence of both signs of V_{zz} with equal probability and a large η .⁸ A covalent cluster model with a well-defined local structure, on the other hand, would lead to a unique sign of V_{zz} . Information on the sign of V_{zz} in an amorphous system eventually can be obtained if one applies an external magnetic field at a temperature far above T_C where the paramagnetic contribution to the effective magnetic hf field B_{eff} is negligible compared to the external field. Figures 1(a) and 1(b) show the simulated ME spectra for $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ in an external magnetic field of $B_{\text{ext}}=5$ T (field direction parallel to γ -ray beam) taking the experimental observed values for ΔE_Q and the line width Γ ,⁴ assuming (i) a random orientation between V_{zz} and B_{ext} , and (ii) $\eta=0$. It can be seen from Fig. 1(a) that an asymmetry in the ME spectrum is observable if (i) V_{zz} has a preferred sign, and (ii) $\eta \neq 0$. Thus the observation of such an asymmetry in a ME spectrum of an amorphous solid in the paramagnetic state in external magnetic field would give additional information on V_{zz} and η . No conclusion can be drawn if the ME spectrum is symmetric, since this can be caused either by the occurrence of both signs in V_{zz} with equal probability or by a large asymmetry parameter η .

We want to mention that the above described method has not yet been applied to a metal-metalloid glass. However, it was successfully used in the study of iron-based oxide glasses.⁹

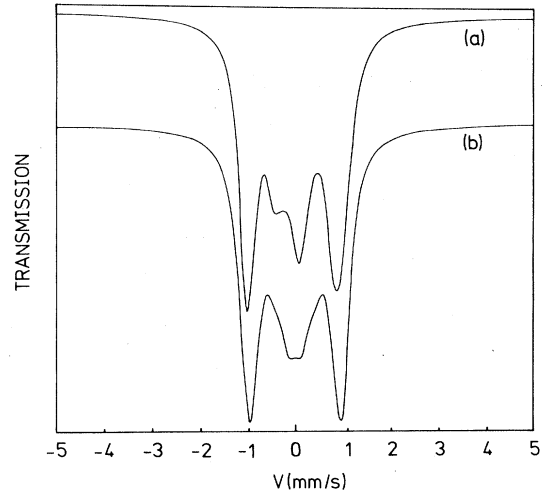


FIG. 1. Simulated ME spectra for $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ in the paramagnetic state with an external magnetic field of $B_{\text{ext}}=5$ T, parallel to the γ -ray direction assuming random orientation between V_{zz} and B_{ext} and $\eta=0$ for two different cases: (a) V_{zz} has a preferred sign ($V_{zz} > 0$), (b) V_{zz} has both signs with equal probability. These spectra can be compared with the measured spectrum in Fig. 4.

IV. EXPERIMENTAL DETAILS

No high-pressure ME-absorption experiments on ⁵⁷Fe containing samples at 4.2 K have been reported so far. The basic problems in high-pressure ME-absorption experiments with the ⁵⁷Fe resonance using B_4C anvils are the following: (i) there is a strong γ -ray absorption due to B_4C , and (ii) B_4C contains ⁵⁷Fe impurities (≤ 1 ppm) which cannot be removed without destroying the mechanical properties of this material. For these reasons Liu and Ingalls,¹⁰ for example, used the following setup: the γ -beam axis is perpendicular to the force-anvil axis avoiding transmission of the γ beam through the B_4C anvils. The disadvantages of this setup are a limited absorber size of ≈ 0.2 mm², the poor solid angle, and a lowest possible absorber temperature of ≈ 20 K. Therefore we have decided to use a high-pressure setup as usually taken for low-temperature ME-absorption experiments with other ME isotopes (e.g., ¹⁵¹Eu, ¹¹⁹Sn) and which is described elsewhere¹¹; the γ -beam axis is parallel to the force-anvil axis, i.e., γ -rays have to be transmitted through the B_4C anvils. In order to correct for the ⁵⁷Fe impurity spectrum of the B_4C anvils each measurement has to be made twice: with the sample [spectrum (a)] and without the sample [spectrum (b)]. All spectra shown have been obtained by subtraction of spectrum (b) from spectrum (a). Owing to the strong γ -ray absorption of the B_4C anvils ($\approx 10\%$ transmission) we have used a 60 mCi ⁵⁷Co:Rh source (≈ 5 mm active diameter) which resulted in a typical counting rate of ≈ 1000 counts per sec measured with a krypton proportional counter. With this setup the absorber (≈ 4 mm diam) together with the source can be held at any controlled temperature between 1.7 and 350 K. Thus we can measure not only the temperature dependence of a high-pressure ⁵⁷Fe ME-absorption spec-

trum but also the pressure dependence of the magnetic ordering temperature T_C , i.e., $\partial T_C/\partial p$, by means of the "thermal-scanning" technique (see also Sec. VC). The pressure calibration was performed *in situ* at 4.2 K with the help of a lead manometer and the known pressure dependence of the superconducting transition temperature of lead.¹²

The ME-absorption experiments with external magnetic field have been done with an applied field of 5 T and with the field direction parallel to the γ -ray beam at an absorber temperature of 300 K. This temperature is ≈ 25 K above T_C and is usually sufficiently high to neglect the paramagnetic contribution to B_{eff} for a pure paramagnetic system of atomic spins with a moment of $\approx 2\mu_B$.¹³ The metallic glasses used in this work were ribbons (width ≈ 0.5 –2 mm, thickness ≈ 20 μm) prepared by the melt-spinning technique at the Central Research Institute of Physics, Budapest, by A. Lovas. The crystalline-phase $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ has been obtained by crystallization of the metallic glass (≈ 1.5 h at 690 K). Thus we have used the *same* sample for the comparison between the amorphous and crystalline state.

V. EXPERIMENTAL RESULTS

A. High-pressure ME-absorption experiments

The ME-absorption spectra of amorphous $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ at 4.2 K and pressures $p=0$ and 36 kbar are given in Figs. 2(a) and 2(b). The spectra were fitted with a magnetically split six-line pattern assuming a Gaussian distribution of the magnetic hf field B_{eff} :

$$p(B_{\text{eff}}) \propto \exp\left\{-\frac{1}{2}[(B_{\text{eff}} - \bar{B}_{\text{eff}})/\Delta B_{\text{eff}}]^2\right\}.$$

\bar{B}_{eff} is the mean value of the hf field distribution, and ΔB_{eff} is the standard deviation of the Gaussian distribution. The spectra of the crystalline sample are shown in

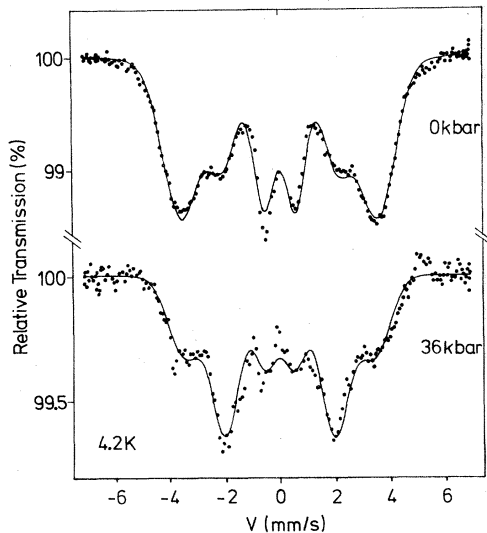


FIG. 2. Mössbauer spectra of amorphous $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ at $T=4.2$ K: (a) at ambient pressure, and (b) at applied pressure ($p=36$ kbar).

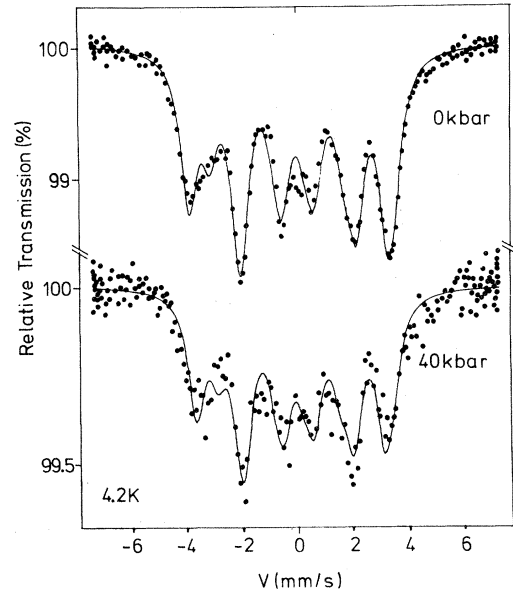


FIG. 3. Mössbauer spectra of crystalline $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ at $T=4.2$ K: (a) at ambient pressure, and (b) at applied pressure ($p=40$ kbar).

Figs. 3(a) and 3(b). They have been fitted with two six-line patterns corresponding to the two inequivalent sites in the orthorhombic Ni_3B structure occupied in a 1:2 ratio.¹⁴ 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. Under high pressure the spin direction is tilted more in the ribbon plane, i.e., off from the γ -ray direction. Thus the intensity of lines 2 and 5 was treated as a free parameters in our fitting procedure. Table I gives the magnetic hf parameters at 4.2 K as obtained from least-squares fits to the measured spectra. The pressure dependence of the isomer shift $S(\partial S/\partial p)$ as well as that of the quadrupole splitting $\Delta E_Q(\partial \Delta E_Q/\partial p)$ have been previously measured in the paramagnetic phases at 300 and 340 K, respectively.⁴

B. ME-absorption experiment in external magnetic field

The ME-absorption spectrum of $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ at 300 K, i.e., in the paramagnetic state, with an external magnetic field of $B_{\text{ext}}=5$ T parallel to the γ -ray direction, can be seen in Fig. 4. This spectrum has to be compared with the theoretical expected spectra shown in Figs. 1(a)

TABLE I. Magnetic hyperfine data at 4.2 K for both amorphous and crystalline $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$. The data are obtained from least-squares fits to the measured spectra.

Sample	p (kbar)	\bar{B}_{eff} (T)	$\partial \ln \bar{B}_{\text{eff}}/\partial p$ (kbar) ⁻¹
Amorphous	0	22.40 ± 0.15	$-(1 \pm 0.4) \times 10^{-3}$
	36	21.6 ± 0.3	
Crystalline	0	21.0 ± 0.2	$-(1.25 \pm 0.35) \times 10^{-3}$
	40	20.0 ± 0.3	

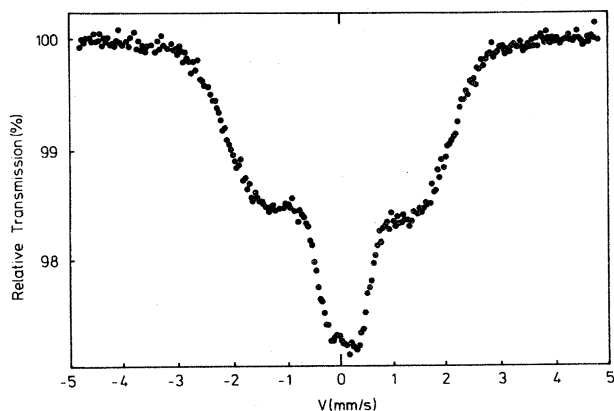


FIG. 4. Mössbauer spectrum of amorphous $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ at 300 K with an external magnetic field $B_{\text{ext}} = 5$ T parallel to the γ -ray direction. This spectrum is to be compared with the simulated spectra in Figs. 1(a) and 1(b).

and 1(b). There is a clear discrepancy between these spectra which must be due to a large paramagnetic contribution to B_{eff} .

C. Thermal scanning experiments

The pressure dependence of the magnetic ordering temperature T_C has been measured by means of the thermal scanning technique.¹⁵ The ME source was moved with the help of a square-wave function generator at constant velocities of ± 0.3 mm/s, corresponding to the approximate positions of the two quadrupole lines in the paramagnetic spectrum. Figure 5 shows the experimental results. The time of measurement for each temperature point was 16 min. The relative changes of the counting rates were of the order of 0.5% (see bars on the left-hand side of the figure). The magnetic ordering temperatures T_C are indicated by arrows. The values of $\partial T_C / \partial p$ are given in Table II.

VI. DISCUSSION

A. Magnetic hf interaction

The pressure dependence of the magnetic hf field B_{eff} at the ^{57}Fe nucleus in $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}_{25}$ is about the same for both the amorphous and the crystalline state (see Table I). This finding is in agreement with that for crystalline and amorphous $\text{Fe}_{75}\text{B}_{25}$ at 300 K.⁴ Using the value for the compressibility of $\kappa = 6 \times 10^{-4}$ kbar⁻¹,¹⁶ we obtain $\partial \ln \bar{B}_{\text{eff}} / \partial \ln V = 1.8 \pm 0.3$ for both the amorphous and crystalline state of $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}_{25}$. This value is $\approx 20\%$ higher than that for $\text{Fe}_{75}\text{B}_{25}$ (Ref. 4) but a factor of ≈ 2 smaller than that for the Metglass[®] M62826A ($\text{Fe}_{32}\text{Ni}_{36}\text{Cr}_{14}\text{P}_{12}\text{B}_6$).¹⁷ The high values of $\partial \ln \bar{B}_{\text{eff}} / \partial \ln V$ in the metal-metalloid glasses compared to that of $\alpha\text{-Fe}$ ¹⁸ and the similarity in these values for the amorphous and crystalline state indicate (i) the importance of Fe-B bonds in these systems, and (ii) similar Fe-B bonding in the amorphous and crystalline state. The consequence of these findings in connection with the local structure of the

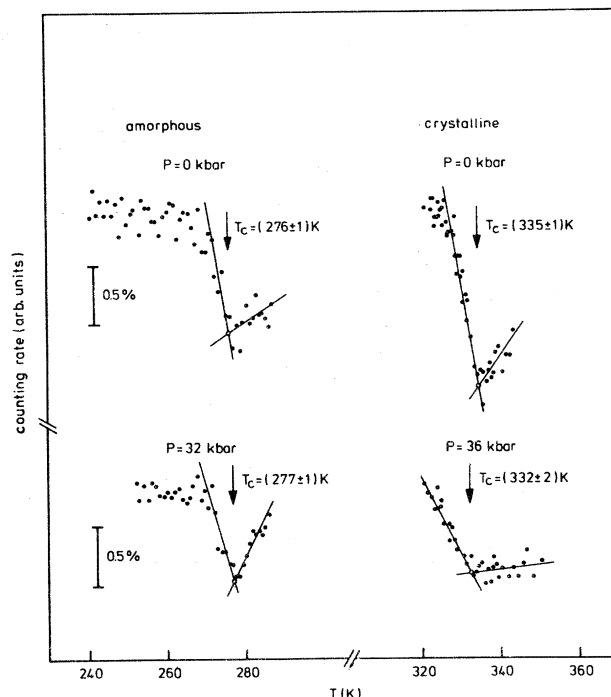


FIG. 5. Pressure dependence of the magnetic ordering temperature T_C measured for both amorphous and crystalline $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ using the thermal-scanning technique. Curie temperatures T_C are indicated by arrows.

amorphous state will be discussed in Sec. VI B.

The ME spectrum with an applied external field at 300 K (see Fig. 4) shows the presence of a large "paramagnetic" contribution to B_{eff} . This can be explained only if one assumes the occurrence of large spin clusters at this temperature. This is in agreement with the results of Kaul¹⁹ who has shown by a detailed analysis of the magnetization versus field isotherms taken above T_C for amorphous $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{80}\text{P}_{14}\text{B}_6$ that for $t = (T - T_C) / T_C \approx 0.1$ the average cluster moment is still of the order $2 \times 10^3 \mu_B$. The average number of clusters as obtained by Kaul is $\approx 1 \times 10^{18} \text{ g}^{-1}$ for $t \approx 0.1$. Thus, one can conclude that in this amorphous alloy for $t \approx 0.1$, approximately 50% of the Fe atoms are sitting in such large spin clusters.

B. Local structure

We have shown in a previous paper⁴ that there is a relation between the fluctuation $\Delta r_{\text{Fe-X}}$ in the interatomic dis-

TABLE II. Pressure dependence of the ordering temperature T_C for both amorphous and crystalline $(\text{Fe}_{0.25}\text{Ni}_{0.75})_3\text{B}$ measured by the thermal-scanning technique.

Sample	p (kbar)	T_C (K)	$\partial T_C / \partial p$ (K kbar ⁻¹)
Amorphous	0	276 ± 1	< 0.03
	32	277 ± 1	
Crystalline	0	335 ± 1	≈ -0.08
	36	332 ± 2	

tances $r_{\text{Fe-X}}$, $(\Delta B_{\text{eff}}/\bar{B}_{\text{eff}})$, and the measured value $\partial \ln \bar{B}_{\text{eff}}/\partial \ln V$ as obtained from high-pressure ME experiments:

$$(\Delta B_{\text{eff}}/\bar{B}_{\text{eff}}) = 3(\partial \ln \bar{B}_{\text{eff}}/\partial \ln V)(\Delta r_{\text{Fe-X}}/r_{\text{Fe-X}}) \quad (1)$$

The essential assumption made in the derivation of this relation is that the magnitude of B_{eff} is governed by one type of bond Fe—X. X can be either a metal atom (Fe or Ni) or the metalloid atom (B). Scattering experiments on isotopically substituted Fe₈₀B₂₀ provide $(\Delta r_{\text{Fe-Fe}}/r_{\text{Fe-Fe}}) = 0.078$ and $(\Delta r_{\text{Fe-B}}/r_{\text{Fe-B}}) \leq 0.047$.²⁰ Taking these data and our measured value $\partial \ln \bar{B}_{\text{eff}}/\partial \ln V = 1.8 \pm 0.3$ we obtain the following two calculated values for $(\Delta B_{\text{eff}}/\bar{B}_{\text{eff}})$ depending on the type of bond which is mainly responsible for the magnitude of B_{eff} :

$$(\Delta B_{\text{eff}}/\bar{B}_{\text{eff}})_{\text{calc}} = 0.42 \quad \text{for } X = \text{Fe(Ni)},$$

$$(\Delta B_{\text{eff}}/\bar{B}_{\text{eff}})_{\text{calc}} \leq 0.25 \quad \text{for } X = \text{B}.$$

These values have to be compared with the measured value

$$(\Delta B_{\text{eff}}/\bar{B}_{\text{eff}})_{\text{meas}} = 0.165.$$

This shows clearly that the Fe-B interaction governs B_{eff} in (Fe_{0.25}Ni_{0.75})₇₅B₂₅. The relative fluctuations $\Delta r_{\text{Fe-B}}/r_{\text{Fe-B}}$ may be even smaller than obtained from x-ray data. A value of $(\Delta r_{\text{Fe-B}}/r_{\text{Fe-B}}) = 0.032$ is obtained from formula (1) if one takes the measured values of $(\Delta B_{\text{eff}}/\bar{B}_{\text{eff}})$ and $(\partial \ln \bar{B}_{\text{eff}}/\partial \ln V)$. This value can be treated as an upper limit, since other fluctuations than $\Delta r_{\text{Fe-B}}$ may give additional contributions to ΔB_{eff} . Such a strong correlation in the Fe-B distances favors the covalent cluster model of Vincze *et al.*,² which assumes well-defined (Fe,Ni,B) clusters, similar to that in orthorhombic (Fe_{0.25}Ni_{0.75})₃B. The quadrupole splitting ΔE_Q , however, is different for amorphous and crystalline (Fe_{0.25}Ni_{0.75})₇₅B₂₅ and cannot be explained by different bond lengths.⁴ ΔE_Q is the only hf parameter which is sensitive to the angular distribution of the nearest neighbors. Thus the difference in ΔE_Q indicates differences in the Fe—B bonding angles. More information on ΔE_Q was supposed to be obtainable from ME experiments where an external magnetic field is applied in the paramagnetic phase. The occurrence of a large paramagnetic contribution to B_{eff} in connection with slow paramagnetic relaxation, however, prevents a reliable analysis of the ME spectrum (see Secs. V A and V I A). There is a small asymmetry present in the ME spectrum (see Fig. 4). It would be very tempting to interpret this asymmetry in terms of a preferred sign of V_{zz} together with a correlation between the direction of V_{zz} and the ribbon plane. Since many other origins for such small asymmetry are possible (for example, a correlation between the isomer shift and B_{eff}), we are anxious to draw any conclusion on V_{zz} from this asymmetry.

C. Pressure dependence of Curie temperature

The pressure dependence of the Curie temperature T_C has already been measured in a variety of amorphous sys-

tems. $\partial T_C/\partial p$ was determined either by susceptibility measurements via the mutual induction method^{21,22} or by the "thermal-scanning" technique.¹⁷ These data together with our results on amorphous and crystalline (Fe_{0.25}Ni_{0.75})₇₅B₂₅ and some data on crystalline (Fe,Ni) alloys are plotted in Fig. 6. The Fe-Ni-alloy data show large $\partial T_C/\partial p$ values (≈ -5 K kbar⁻¹) and follow a T_C^{-1} law as predicted by Wagner and Wohlfarth²³ for magnetic homogeneous alloys. The $\partial T_C/\partial p$ values of the metal-metalloid glasses are more than an order of magnitude smaller (≈ -0.5 K kbar⁻¹).

A careful analysis of $\partial \bar{B}_{\text{eff}}/\partial p$ in Fe₇₅B₂₅ at 300 K has to take into account the decrease of T_C with pressure. We had assumed $\partial T_C/\partial p$ to be ≈ -0.5 K/kbar. A linear extrapolation of the data in Fig. 6 to $T_C \approx 725$ K for Fe₇₅B₂₅ gives $\partial T_C/\partial p \approx -0.5$ K/kbar in agreement with our previous assumption.⁴ The tendency that $\partial T_C/\partial p$ in Fe,Ni-containing metal-metalloid glasses decreases with increasing Ni concentration, i.e., with decreasing T_C , can be described in a first approximation by $\partial T_C/\partial p \propto -T_C$. This is in agreement with the theoretical prediction for $\partial T_C/\partial p$ in very heterogeneous magnetic alloys.²³ An exception is Fe₃₂Ni₃₆Cr₁₄P₁₂B₆ (Ref. 17) which is the only metallic glass studied which contains Cr in addition to Fe and Ni. We do not know if this is the reason for its exceptional behavior but this should be tested by further $\partial T_C/\partial p$ measurements on Cr containing metal-metalloid glasses.

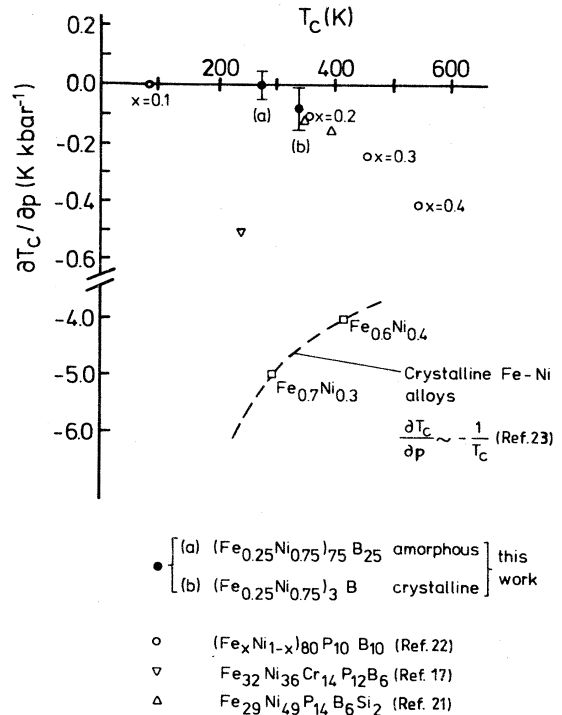


FIG. 6. $\partial T_C/\partial p$ plotted as a function of T_C for amorphous and crystalline (Fe_{0.25}Ni_{0.75})₃B. For comparison, values for other (Fe,Ni)-containing systems are also presented.

VII. CONCLUSION

The high-pressure ME experiments at 4.2 K on amorphous and crystalline $(\text{Fe}_{0.25}\text{Ni}_{0.75})_{75}\text{B}_{25}$ confirm our conclusions about the local atomic structure in this type of metallic glasses drawn from similar experiments at 300 K on amorphous and crystalline $\text{Fe}_{75}\text{B}_{25}$: The similar response of all hyperfine parameters observed for both the amorphous and crystalline alloy with decreasing volume supports those models which assume that a similar amorphous and crystalline local structure is a good approximation in the $(\text{Fe}_{1-x}\text{Ni}_x)_{75}\text{B}_{25}$ system. A much smaller relative distribution of the metal-metalloid distances compared to the relative distribution of the metal-metal distances has been predicted in our previous paper and has now been established by scattering experiments on isotopically substituted $\text{Fe}_{80}\text{B}_{20}$. These scattering data together with the measured distance sensitivity of the hyperfine field \bar{B}_{eff} as obtained from the high-pressure ME experiments show clearly that the observed narrow hyperfine field distribution ($\Delta B_{\text{eff}}/\bar{B}_{\text{eff}} \approx 16\%$) can only be explained if the magnitude of B_{eff} is mainly determined by the metal-metalloid bonds.

ME experiments with an applied external magnetic field in the paramagnetic state are not very helpful for deciding if there is a preferred sign of V_{zz} in this type of metallic

glasses. The difficulty in analyzing such spectra is the occurrence of large spin clusters and thus a large paramagnetic contribution to B_{eff} above T_C . Such experiments, therefore, have to be carried out far above T_C , which will not be possible for most of the metal-metalloid glasses due to the onset of crystallization. The measured pressure dependence of T_C is in qualitative agreement with the theoretical approach by Wagner and Wohlfarth based on a Landau-Ginzburg formalism.

The successful application of the high-pressure ME-technique for studying the local structure of metal-metalloid glasses gives some confidence that the extension of such experiments to pure metallic glasses like $\text{Fe}_{1-x}\text{Zr}_x$ may be similarly informative. Such experiments are under way.

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