KFKI-1983-57

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METALLIC GLASSES: A NMR STUDY

Hungarian Academy of Sciences

CENTRAL
RESEARCH
INSTITUTE FOR
PHYSICS

BUDAPEST

2017

LOCAL BORON ENVIRONMENT IN $Ni_{100-x}B_x$ METALLIC GLASSES: A NMR STUDY

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ABSTRACT

From the analysis of the ^{11}B NMR spectra in a-Ni$_{100-x}$B$_x$ (18.5<x≤40) the electric field gradient (EFG) components on the B sites and their distributions are deduced, giving an insight into the local atomic arrangements. For x = 18.5 and x = 40, one finds relatively narrow distributions of the EFG components indicating weak fluctuations of the bonding angles, distances and nature of the atoms in the B coordination shell. The comparison with the compositionally closest nickel borides (Ni$_3$B and Ni$_4$B$_3$) immediately suggests that the local structure around B is similar in these glasses and in the related crytals i.e. nickel trigonal prisms (6 Ni) whose rectangular faces are capped by 3 Ni (Ni$_3$B) or 3 Ni/B (Ni$_4$B$_3$). For intermediate concentrations the EFG components distributions are found significantly broader and comparable with those expected from random packing of spheres. However, the continuous evolution of the NMR spectra shape with increasing B content rather suggests an admixture of c-Ni$_3$B like and c-Ni$_4$B$_3$ like B local environment i.e. when B concentration increases more prisms share rectangular faces allowing boron - boron contact as in c-Ni$_4$B$_3$. No sign of a B coordination shell similar to that in c-Ni$_2$B (8 Ni anticubes + 2 B) is found in the glasses. Measurements of transverse relaxation times T$_2$, which reflect essentially the B-B boundings, qualitatively support these conclusions.

АННОТАЦИЯ

На основе изучения ЯМР-спектров аморфных сплавов Ni$_{100-x}$B$_x$(18,5<x<40) определены как компоненты градиента электрического поля (ГЭП) в местах атомов B, так и их распределения для изучения локального упорядочения атомов. В случае содержания бора 18,5 и 40 ат.% было найдено узкое распределение компонентов ГЭП, что указывает на небольшую флуктуацию углов связи, расстояний и видов соседних атомов в окрестности атомов B. Сравнение с кристаллическими боридами никеля (c-Ni$_3$B и c-Ni$_4$B$_3$), имеющими похожий состав, позволяет сделать вывод о том, что локальная структура в окрестности атомов B одинакова в металлических стеклах и аналогичных кристаллических материалах, т.е. состоят из тригональных призм, в вершинах которых находятся 6 атомов Ni, над прямоугольными сторонами которых расположены 3 Ni (Ni$_3$B) или Ni/B (Ni$_4$B$_3$). В случае переходных концентраций бора компоненты ГЭП имели значительно более широкое распределение, соизмеримое по ширине с ожидаемой по структуре плотных случайных упаковок твердых сфер. Однако, непрерывное изменение формы ЯМР-спектров с увеличением содержания бора указывает скорее на наличие смеси c-Ni$_3$B-образных и c-Ni$_4$B$_3$-образных локальных окружений в окрестности атомов B, т.е. с увеличением содержания бора все большее число призм будет иметь общую прямоугольную сторону, что приводит к образованию бор-бор ближайших пар соседей, как в случае с c-Ni$_4$B$_3$. Координационные сферы, аналогичные найденным в c-Ni$_2$B, в металлических стеклах не обнаружены. Измерения времен релаксации T$_2$, отражающих B-B связи, дают качественное подтверждение этих выводов.

KIVONAT

Amorf Ni$_{100-x}$B$_x$ ötvözetek (18,5<x<40) ^{11}B NMR spektrumainak vizsgálata alapján meghatároztuk az elektromos térgradiens (EFG) komponenseit a B helyeken és eloszlásukat a lokális atomelrendeződés tanulmányozása céljából. 18,5 és 40 at.% bórtartalomnál azt találtuk, hogy az EFG komponensek eloszlása keskeny, ami arra utal, hogy a kötési szögek, távolságok és a szomszéd atomok fajtája a B atomok körül csak kevéssé fluktuál. Az összetétel szerint legközelebb eső kristályos nikkelboridokkal (c-Ni$_3$B, ill. c-Ni$_4$B$_3$) való összehasonlitásból arra következtetünk, hogy a B atomok körüli lokális szerkezet hasonló ezekben a fémüvegekben és a megfelelő kristályos anyagokban, nevezetesen 6 Ni atomból álló trigonális prizmák alkotják, amelyek téglalap alaku oldallapjai fölött 3 Ni (Ni$_3$B) vagy 3 Ni/B (Ni$_4$B$_3$) atom helyezkedik el. Közbenső bórtartalmaknál az EFG komponensek eloszlását lényegesen szélesebbnek találtuk, összemérhetőek voltak a merev gömbök véletlenszerü pakolásából várható szélességgel. Az NMR spektrumok alakjának folyamatos változása növekvő bórtartalommal azonban azt sugallja inkább, hogy c-Ni$_3$B-szerü és c-Ni$_4$B$_3$-szerü lokális B környezetek keverékével van itt dolgunk, azaz amint a bórtartalom nő, egyre több prizmának lesz közös a téglalap alaku oldallapja a szomszédjával, ami lehetővé teszi, hogy bór-bór elsőszomszédok is létrejöjjenek, mint a c-Ni$_4$B$_3$ esetében. Nem találtuk semmi jelét annak, hogy a fémüvegekben előfordulnának a c-Ni$_2$B-ben találhatóhoz hasonló B koordinációs héjak. A lényegében a B-B kapcsolatokat tükröző T$_2$ relaxációs idők mérési eredményei kvalitative alátámasztották ezeket a következtetéseket.

I. INTRODUCTION

Studies of the crystal field parameters in amorphous materials have proved useful for the understanding of the amorphous structure [1-2] as they give informations on the symmetry properties of the local structure while usual spectroscopic techniques essentially give informations about distances. NMR has been widely used for that purpose in insulating glasses [3]. For amorphous metals a previous NMR study in a-La$_{75}$Ga$_{25}$, a-Mo$_{70}$B$_{30}$ and a-Ni$_{78}$P$_{14}$B$_8$ has shown that their structure retains to a significant extent the local symmetry around the glass former prevailing in the corresponding crystalline materials (c-La$_3$Ga: cubic; c-Mo$_2$B: uniaxial; c-Ni$_3$B: non uniaxial) [4].

The present study has been performed in two-component metal-metalloid glasses: a-Ni$_{100-x}$B$_x$ for an extended concentration range ($18.5 \leq x \leq 40$) which includes compositions close to the crystalline nickel borides: c-Ni$_3$B, c-Ni$_2$B and c-Ni$_4$B$_3$. The obvious purpose of this work was to study the modifications of the amorphous structure with varying metalloid concentration and to compare it with that of the crystalline counterparts.

Most of the informations on the amorphous structure were obtained in this work through the study of quadrupolar interactions between the nuclear quadrupole moment of ^{11}B ($I = 3/2$) and the local electric field gradient (EFG) whose symmetry reflects that of the local environment of the probe nucleus. The traceless EFG tensor is determined by the quadrupolar frequency $\nu_Q = 3e^2qQ/2I(2I+1)\hbar$ (proportional to its largest eigenvalue $eq = V_{zz}$) and by a dimensionless coefficient $\eta = |V_{xx} - V_{yy}|/|V_{zz}|$. The asymmetry parameter η is a measure of the deviation from an uniaxial local symmetry (which for $\eta = 0$) and ν_Q is a measure of the deviation from cubic symmetry (which for $V_{xx} = V_{yy} = V_{zz} = 0$). As shown on Fig. 1, the NMR spectrum shape is very sensitive to ν_Q and η and these values can usually be obtained directly from the spectrum in crystalline materials. In amorphous materials fluctuations of the local environment from site to site rather smear off the details of the spectrum and although the local symmetry of the EFG (cubic like, uniaxial or non uniaxial) can be qualitatively deduced directly, computer fits are needed for quantitative comparisons.

Some more information was obtained through the measurement of the transverse relaxation time T_2 which is dominated by B nuclei spin-spin interactions and hence related mostly to B-B bondings. As a major conclusion, this study
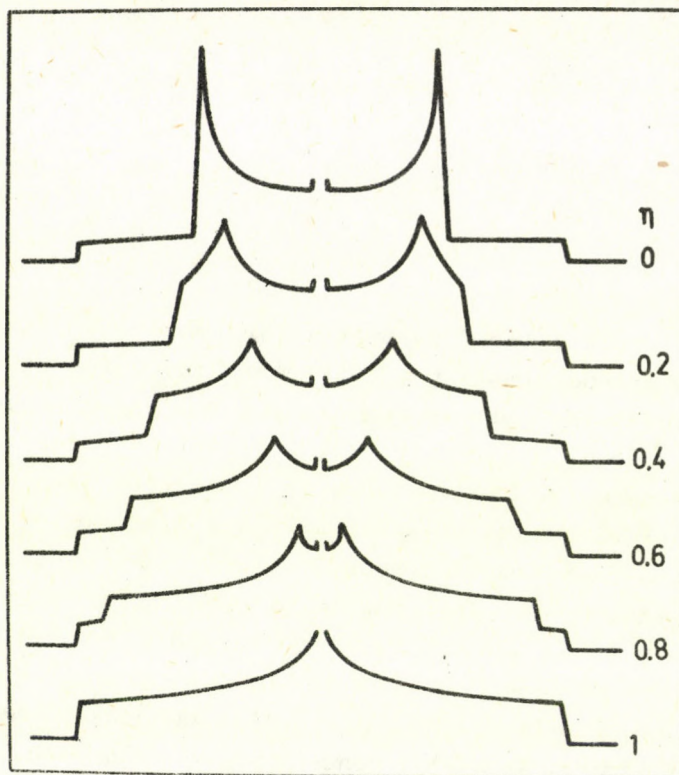
Fig. 1.

Unbroadened NMR "powder" spectra for η varying from 0 to 1.

shows that B atoms in a-Ni$_{100-x}$B$_x$ glasses are most probably surrounded by
nickel trigonal prisms as in c-Ni$_3$B and c-Ni$_4$B$_3$ (orthorhombic); the increase
of the B concentration would be accommodated by changes in the packing of
the prisms allowing more B-B bondings.

II. SAMPLE PREPARATION AND EXPERIMENT

a-Ni$_{100-x}$B$_x$ samples were prepared by rapid quenching (melt spinning).
They could be obtained amorphous (as checked by X-ray diffraction) around
x = 18.5 (eutectic composition), x = 25 and on a broader concentration range
from x = 31 (second eutectic) to x = 40. Samples with high B content are
rather brittle; this was previously mentioned by Donald and Davies [5] and
attributed to directional B-B covalent bondings.

Crystalline samples were prepared by sintering of the elements in sealed
quartz tube; for c-Ni$_4$B$_3$ there exist two allotropic varieties, one orthorhombic
on the low B side and one monoclinic on the high B content side. The former
one was synthetized for comparison purpose since amorphous samples have lower
B content than 43 at %.

NMR spectra of the ^{11}B nucleus (I = 3/2) were observed on a conventional

pulsed NMR spectrometer at ν = 16.592 MHz. They were obtained from integral spin echo intensity vs external field. T_2 was measured conventionally through the decay of the spin echo intensity vs delay between $\pi/2 - \pi$ pulses. Measurements were carried out at 4.2 K except for a-Ni$_{81.5}$B$_{18.5}$ which for the strong magnetic broadening at low temperatures precluded accurate observations.

III.   RESULTS AND ANALYSIS

a) Spectra and EFG parameters

The experimental spectra presented on Fig. 2 (glasses) and Fig. 3 (crystalline compounds) indicate obvious similarities between the EFG's around
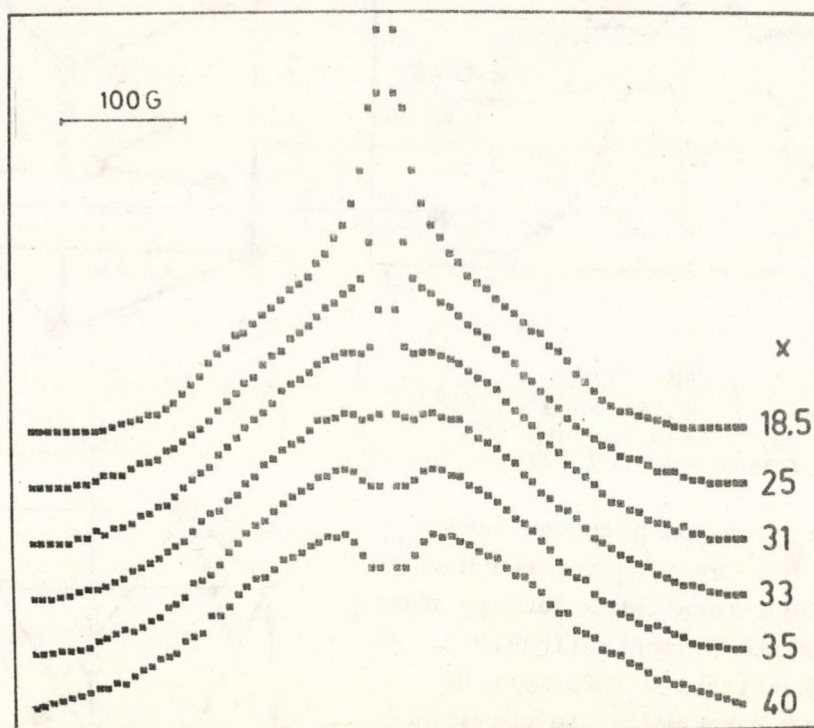

Fig. 2.
Experimental NMR spectra in a-Ni$_{100-x}$B$_x$ samples.
All spectra T = 4.2 K except x = 18.5 (100 K) [11].

boron in the glasses for x = 18.5 and 40 and those in c-Ni$_3$B and c-Ni$_4$B$_3$, respectively. But the uniaxial symmetry of the EFG in c-Ni$_2$B is not found in the amorphous modification and rather a continuous evolution of the spectra shape is observed with increasing B content. This observation indicates that the average boron local environment changes progressively in the glasses while in the crystalline compounds the B coordination shell is quite different in
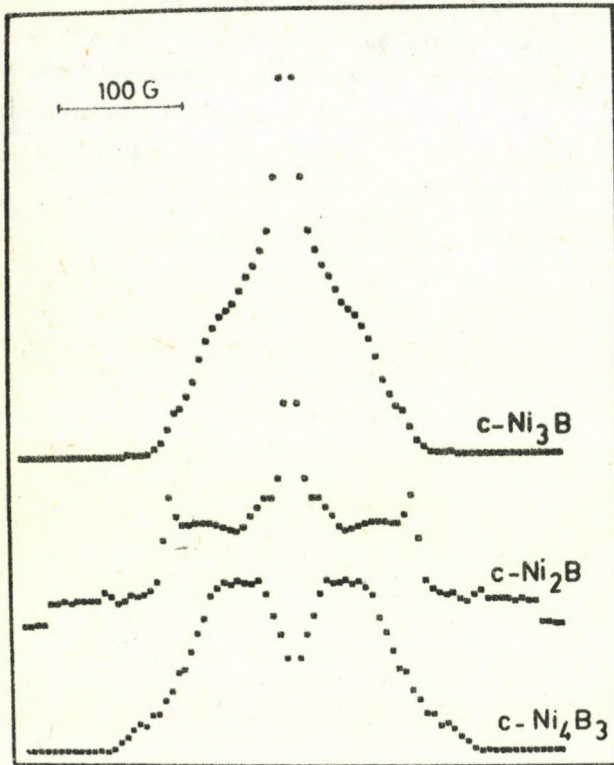
c-Ni$_2$B [anticubes of (8 Ni+2 B) in a tetragonal I$_4$/mcm structure] and in c-Ni$_3$B (trigonal prisms of 6 Ni and 3 Ni at pyramid apices in an orthorhombic Pnma structure) or in c-Ni$_4$B$_3$ (trigonal prisms of 6 Ni and 3 Ni or B at pyramid apices in Pnma structure) (Fig. 4). These qualitative remarks suggest that the boron coordination in the glasses could closely resemble that of B
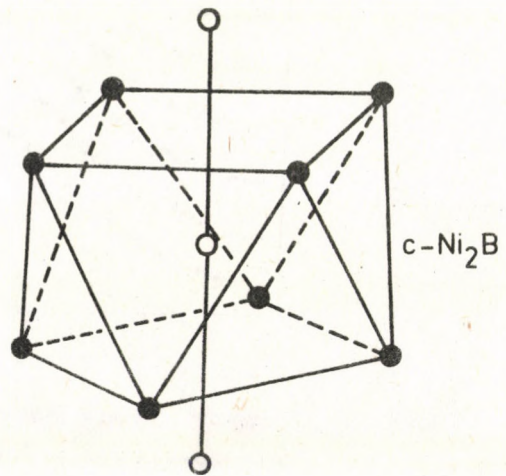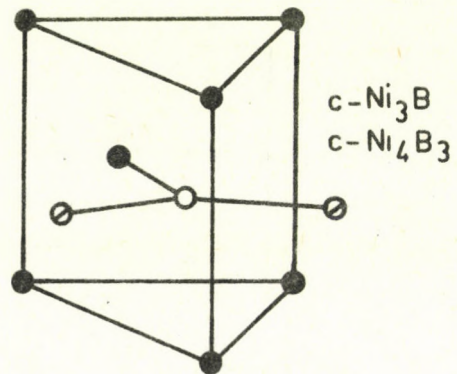

Fig. 3.

Experimental NMR spectra in c-Ni$_3$B, c-Ni$_2$B and c-Ni$_4$B$_3$ (orthorhombic) [11].

c-Ni$_3$B
c-Ni$_4$B$_3$

in c-Ni$_3$B for the low B concentration and that of B in c-Ni$_4$B$_3$ for the high B content and interpolates between them for intermediate concentrations.

More quantitative informations about the EFG parameters are obtained through computer simulation of the experimental spectra. The relevant parameters for the fit are the EFG reduced components ($\bar{\nu}_Q$ and η) and, for the amorphous samples, the rms halfwidth σ of the distribution of the EFG strength ν_Q (or the more convenient ratio $\sigma/\bar{\nu}_Q$ which measures the degree of disorder). Although the asymmetry parameter η certainly fluctuates from site to site in the glasses, no significant improvement of the fits

c-Ni$_2$B

Fig. 4.

*Boron coordination shell in c-Ni$_2$B and c-Ni$_3$B or c-Ni$_4$B$_3$
o: boron; •: Ni; ◐: Ni (in c-Ni$_3$B or for B$_{III}$ in c-Ni$_4$B$_3$), B$_I$ or B$_{II}$ (for B$_I$ or B$_{II}$, respectively, in c-Ni$_4$B$_3$).*

is observed using distributions of η and the shape of the simulated spectra is found to be very insensitive to that distribution except for very broad ones. Thus no systematic attempt to introduce such distribution was made but experimental spectra were compared with the one that would result from the broad distributions of ν_Q and η computed for random packed networks of spheres by Czjzek (1 size) [1] and Takács (2 sizes + metalloid-metalloid avoidance [6], both computations giving very similar distributions shapes. A reason for the weak influence of η distribution on the spectrum shape may be due to the fact that a non-zero η value already implies a distribution of EFG strength in the plane perpendicular to its principal axis; indeed η and $\sigma/\bar{\nu}_Q$ are found interdependent in the fits in the sense that constraining η to a higher value reduces the computed $\sigma/\bar{\nu}_Q$ and vice versa.

We shall first present the results for the crystalline compounds, then for the glasses with $x = 18.5$ and $x = 40$ of which analysis is rather unambiguous and finally for the glasses with intermediate concentrations.

Crystalline nickel borides

The value for ν_Q and η in these compounds are presented in Table I.

Table I.

EFG parameters around B in crystalline nickel borides

Compound		ν_Q	η
c-Ni$_3$B		180 ± 10 kHz	0.6 ± 0.05
c-Ni$_2$B		360 ± 10 kHz	0
c-Ni$_4$B$_3$ (ortho)	B$_I$ or B$_{II}$	$\{230 \pm 20$ kHz	$\begin{cases} 0.2 \pm 0.1 \\ 0.4 \pm 0.1 \end{cases}$
	B$_{III}$	$\{190 \pm 30$ kHz	0.5 ± 0.1

In c-Ni$_3$B and c-Ni$_2$B, these values are obtained directly from the spectra. For c-Ni$_4$B$_3$ the situation is more complex due to the presence of three different crystallographic B sites and we had to use computer simulation to determine the 6 different EFG parameters, as described below. First the highest value for ν_Q is obtained from the overall width of the spectrum; from the step heights at both ends of the spectra it was deduced that this highest ν_Q corresponds to two sites among the three different ones. These results are independent of the values for η's. Then from the examination of the boron

coordination shell for the three sites it was presumed that the third site corresponds to B with no B nearest neighbours (B_{III}). Indeed it is highly probable that the highest ν_Q value corresponds to the two sites with two B nearest neighbours (B_I and B_{II}), a situation being similar to that of B in c-Ni_2B; a calculation of the EFG in a point charge model (PCM) supports this assumption since it yields comparable ν_Q's for B_I and B_{II} and a much lower ν_Q for B_{III} emphasizing the role of the two B nearest neighbours. Trial values of η's on B_I and B_{II} sites were consecutively obtained by a first fit assuming that ν_Q and η on B_{III} are the same as in c-Ni_3B (same environment). The values for η and ν_Q on B_{III} and η's on B_I and B_{II} were obtained in the final refinement (Fig. 5).
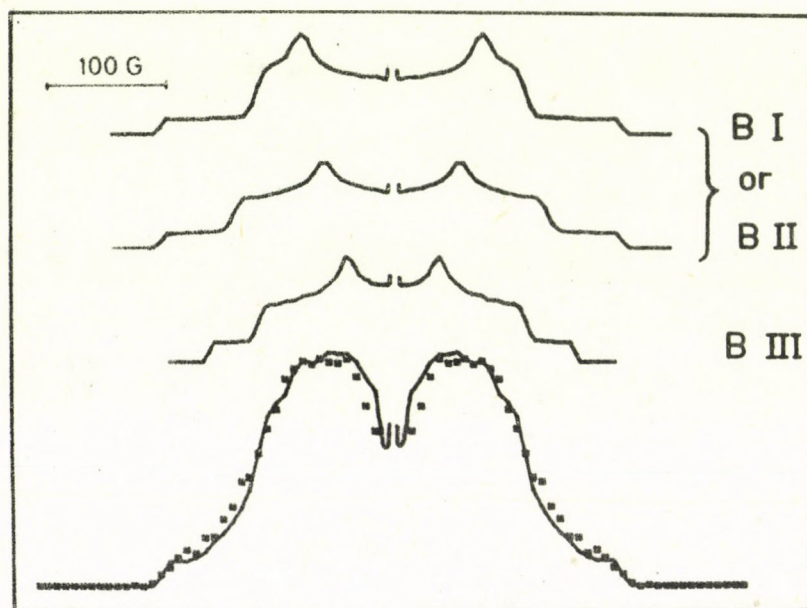
Fig. 5.

B_I, B_{II} and B_{III} NMR subspectra as obtained by fit of the B NMR spectrum in c-Ni_4B_3.

a-$Ni_{81.5}B_{18.5}$
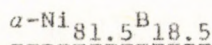
For this sample, a significant overall Lorentzian broadening had to be introduced to reproduce the central line width (HWHM = 15 G); this broadening results from magnetic homogeneities in the sample probably due to precipitation of small nickel particles (about 3 % of the total volume) [7]. Then an excellent fit of the spectrum is obtained for $\bar{\nu}_Q$ = 230 $\pm$ 10 kHz, η=0.6$\pm$0.1 and $\sigma/\bar{\nu}_Q \leq 0.15$ (Fig. 6). Comparable values were obtained previously [4] for B in a-$Ni_{78}P_{14}B_8$ (220 $\pm$ 20 kHz; 0.65 $\pm$ 0.15; 0.25 $\pm$ 0.05 for $\bar{\nu}_Q$, η and $\sigma/\bar{\nu}_Q$); however the degree of disorder $\sigma/\bar{\nu}_Q$ is slightly higher in this last
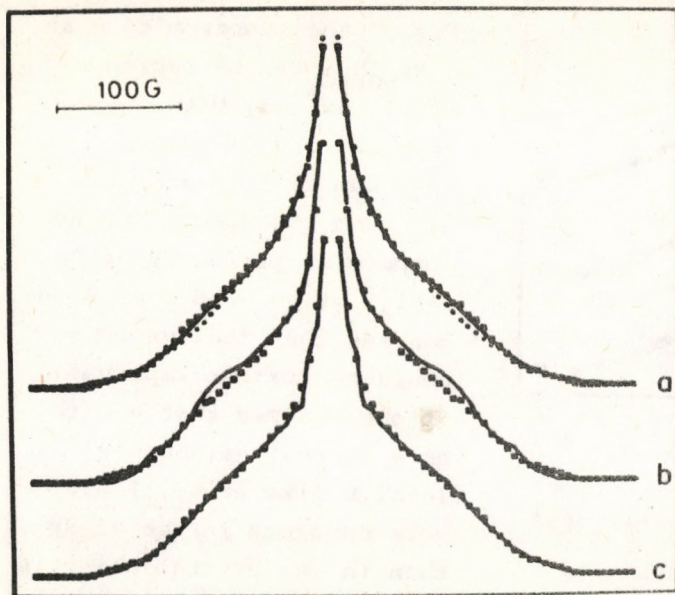
Fig. 6.

B experimental NMR spectrum in a-Ni$_{81.5}$B$_{18.5}$ (crosses). Full line: (a) Simulated spectrum for $\bar{\nu}_Q$=230 kHz, η=0.6, $\sigma/\bar{\nu}_Q$=0.15 (fit includes Lorentzian magnetic broadening). (Dots : id. except $\sigma/\bar{\nu}_Q$=0.25). (b) B experimental spectrum in c-Ni$_3$B expanded 35 % along the horizontal axis. (c) Same as (b) except a 15 % rms width distribution of the expansion factor is added.

sample certainly because of chemical disorder introduced by the presence of two metalloids. The comparison with c-Ni$_3$B shows that the symmetry of the EFG on B sites is the same in the crystalline and the glassy compounds (η = 0.6). The strength of the EFG is however 30 to 40 % higher in the glass. Indeed the spectrum in c-Ni$_3$B compares quite well with that in a-Ni$_{81.5}$B$_{18.5}$ once expanded 35 % horizontally to take into account the higher $\bar{\nu}_Q$; once added a distribution of the expansion factor (to simulate the distribution of ν_Q's) both spectra can be superimposed; this obviously confirms the direct fit. Furthermore, one should note that these results are not consistent with random packed structure calculations: firstly $\sigma/\bar{\nu}_Q$ is much lower than the value predicted for RPN ($\sigma/\bar{\nu}_Q \simeq 0.3$ for spheres of equal radius to $\sigma/\bar{\nu}_Q \simeq 0.5$ for atomic radii ratios r metal/r metalloid = 1.4 which is our case) and secondly, the relatively sharp decrease of the signal at both ends of the spectrum which results from high but weakly fluctuating η cannot be observed for a RPN.

a-Ni$_{60}$B$_{40}$
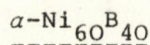
For this sample a good fit was obtained for $\bar{\nu}_Q$ = 300 $\pm$ 30 kHz; η = 0.4 $\pm$ $\pm$ 0.1 and $\sigma/\bar{\nu}_Q$ = 0.25 (Fig. 7). The lower value for η could be predicted from the dips close to the central peak which are not compatible with the distribution of η's computed in a random packed network. These values again compare well with those found in c-Ni$_4$B$_3$ ($\bar{\nu}_Q$ = 230 kHz, $\bar{\eta}$ = 0.37) although again $\bar{\nu}_Q$ is 30 % to 40 % higher in the glass than in the crystal. The value for $\sigma/\bar{\nu}_Q$ is also slightly higher than in a-Ni$_{81.5}$B$_{18.5}$ but one should note that ν_Q also fluctuates from site to site in c-Ni$_4$B$_3$ ($\sigma/\bar{\nu}_Q$ = 0.1). The quality of the fit could obviously be improved using distributions around several $\bar{\nu}_Q$ but this would give ambiguous results owing to the number of independent parameters. Therefore a direct comparison with the spectrum in c-Ni$_4$B$_3$ has also been
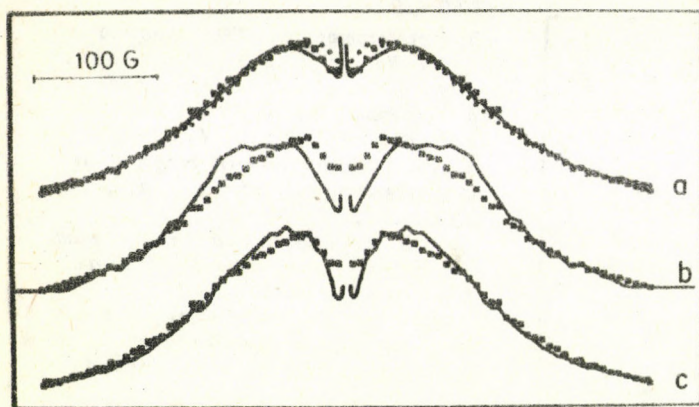
Fig. 7.

Fig. 7.
B experimental NMR spectrum in a-Ni$_{60}$B$_{40}$
(crosses).
Full line: (a) Simulated spectrum for
$\bar{\nu}_Q$ = 300 kHz, η = 0.4,
$\sigma/\bar{\nu}_Q$ = 0.25. (Dots: id. except $\sigma/\bar{\nu}_Q$ = 0.3).
(b) B experimental spectrum in c-Ni$_4$B$_3$
expanded 35 % along the horizontal axis.
(c) Same as (b) except a 25 % rms width
distribution of the expansion factor is added.

performed: as shown in Fig. 7 the spectrum of B in a-Ni$_{60}$B$_{40}$ can be reproduced nearly exactly with the expanded and broadened spectrum of B in c-Ni$_4$B$_3$. Although the spectra do not compare as perfectly as for a-Ni$_{81.5}$B$_{18.5}$ and c-Ni$_3$B one can see that the agreement could be further improved if one assumes that B with no B nearest neighbours (c-Ni$_3$B like or B$_{III}$) are more numerous in the glass than in the crystal which is consistent with the lower B content in the glass.

Intermediate concentrations

For x = 25, although this sample corresponds exactly to c-Ni$_3$B the spectrum shape already deviates more from the crystalline cace than in a-Ni$_{81.5}$B$_{18.5}$ and simulations show a higher disorder ($\sigma/\bar{\nu}_Q \simeq 0.3$).

For x = 33, the spectrum shape cannot be related in any way to that for c-Ni$_2$B: simulations show high non uniaxiality ($\eta \simeq 0.5$) and also high disorder.

The spectra for x = 25, 31, 33 are the closest to the one that would result from random packing. Indeed an agreement is found between the shapes of the spectrum for x = 25 and the spectrum computed for a random packed network (RPN) if the dipolar broadening of the central line is not taken into account in the fit. This agreement, however, is fortuitous.

Taking advantage of the shorter T$_2$ on the central line than on the quadrupolar wings (see next section) one can strongly reduce the contribution to the spectrum of the central line (1/2 $\leftrightarrow$ - 1/2 transition). In such a case one sees that the spectrum corresponding to the $\pm$ 3/2 $\leftrightarrow$ $\pm$ 1/2 transitions is much flatter close to the center and the misfit with the RPN spectrum is more evident (Fig. 8).

Actually, as mentioned before the spectrum shape changes progressively with increasing B content and dips on each side of the central line become apparent for x = 33 and evident for x = 35, indicating a reduction of the average η from 0.6 (x = 18.5) to 0.4 (x = 40). Indeed excellent fit of the spectra for 25 $\leq$ x $\leq$ 35 can be obtained with a weighted sum of the spectra for x = 18.5 and 40 (Fig. 9).

Fig. 8.

(a) B experimental NMR spectrum in a-Ni$_{75}$B$_{25}$ (crosses).
Full line: spectrum simulated with the ν_Q and η distributions computed for a random packed network (no other broadening added).
(b) Same as above except the central line (1/2$\leftrightarrow$ -1/2 transition) is experimentally reduced 10 times with respect to the quadrupole wings ($\pm$3/2$\leftrightarrow$ $\pm$1/2 transitions) (see text).
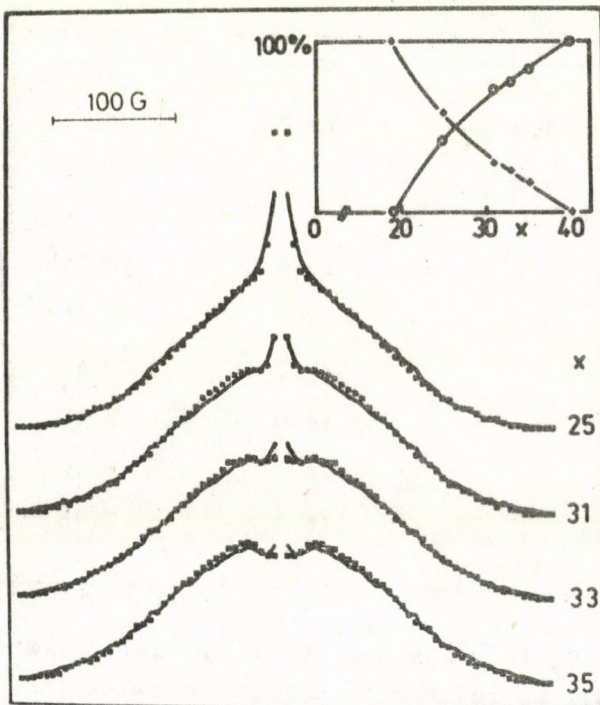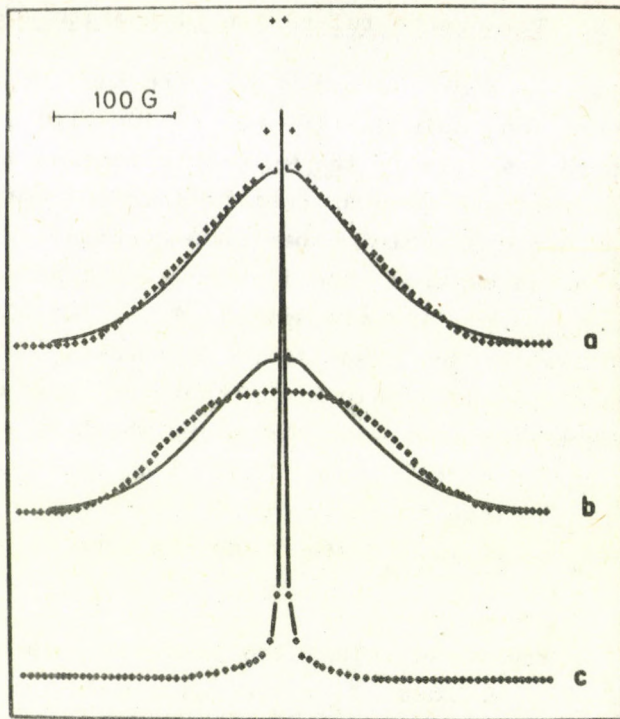(c) Central line shape deduced by substracting (b) from (a) (reduced 2.5 times with respect to a and b).

Fig. 9.

Fit of the spectra in a-Ni$_{100-x}$B$_x$ (25 < x < 35) with a weighted sum of spectra observed in a-Ni$_{81.5}$B$_{18.5}$ and a-Ni$_{60}$B$_{40}$.
Inset: relative intensities of the a-Ni$_{81.5}$B$_{18.5}$ (+) and a-Ni$_{60}$B$_{40}$ (o) spectra as function of B content.

b) Transverse relaxation time measurements

In the nickel borides owing to the very low nuclear moment of Ni and the very long spin lattice relaxation times, the transverse relaxation T_2 reflects essentially the spin-spin interaction between B nuclei. Hence this measurement can give an insight into the boron-boron distances and arrangements. Since B nuclei experience quadrupole interaction, T_2 has been measured on the central line ($1/2 \leftrightarrow -1/2$ transition: T_{2c}) and on the quadrupolar wings ($\pm 3/2 \leftrightarrow \pm 1/2$ transition: T_{2w}). For all samples the transverse nuclear magnetization decay was found exponential (except perhaps for very short times $\tau < 50$ µs). This means that the dipolar line broadening results in a (truncated) Lorentzian like shape which is clearly observed in c-Ni_2B (broad foot of the central line, Fig. 3) or in a-$Ni_{75}B_{25}$ (Fig. 8) and explains why the peaks close to the central line for $\eta = 0.6$ are not resolved in c-Ni_3B. Thus T_2's are well defined and the results are summarized in Table II.

Table II.

Transverse relaxation times in crystalline and glassy nickel
borides (T_{2c}: central line; T_{2w}: quadrupolar wings);
$<r_{BB}>$: average boron-boron distance and x: boron concentration

Compound	T_{2c} (µs)	T_{2w} (µs)	$T_{2c}/<r_{BB}>^3$ (µs/$Å^{+3}$)	T_{2c} x/100 (µs)	T_{2c}/T_{2w}
c-Ni_3B	580 $\pm$ 50	890 $\pm$ 100	15.4 $\pm$ 2	14.5	0.65
c-Ni_2B	380 $\pm$ 40	430 $\pm$ 80	14.4 $\pm$ 2	13.0	0.88
c-Ni_4B_3	330 $\pm$ 40	590 $\pm$ 100	16.9 $\pm$ 2	14.0	0.56
a-$Ni_{81.5}B_{18.5}$	800 $\pm$ 100	1800 $\pm$ 400		15.0	(0.45)
a-$Ni_{75}B_{25}$	540 $\pm$ 50	1410 $\pm$ 100		13.5	0.36
a-$Ni_{69}B_{31}$	515 $\pm$ 50	1270 $\pm$ 100		16.0	0.41
a-$Ni_{67}B_{33}$	425 $\pm$ 40	945 $\pm$ 100		14.0	0.45
a-$Ni_{65}B_{35}$	400 $\pm$ 40	820 $\pm$ 100		14.0	0.48
a-$Ni_{60}B_{40}$	390 $\pm$ 40	810 $\pm$ 100		16.0	0.48

Because of the Lorentzian like shape, T_2 is a measure of the inverse halfwidth at half maximum (HWHM) which can hardly be related to the rms halfwidth of the dipolar broadening unless the fourth moment of the dipolar broadening could be computed. This is totally unachievable in such complex structure for powder samples and with quadrupolar interaction. Unfortunately the HWHM

is much less sensitive to the distribution of distances than the rms width (or the second moment). However, qualitative conclusions can be drawn from the comparison between glasses and crystals.

First, as shown on Table II, T_{2c} scales with the cube of the average B-B distance in crystalline materials and also with the inverse boron concentration in all samples. This shows that the average B-B distances are the same in the glasses and in the crystal of same composition.

Second, T_{2w} is usually much longer than T_{2c} except in c-Ni_2B. This is qualitatively understood in the following way: in c-Ni_2B all boron spins are like spin, i.e. the central B atom and all its B neighbours experience the same EFG (strength and orientation), thus the three different frequencies for the three transitions are the same for the central nucleus and for its neighbours resulting in an efficient dipolar coupling whatever transition is concerned; on the contrary, only part of the B spins in the neighbourhood of the central atom are like spins in c-Ni_3B and none in c-Ni_4B_3; others are unlike spins experiencing EFG with different orientation (Ni_3B) and/or different strength (Ni_4B_3). This reduces much more the dipolar transition probability for $\pm 3/2 \leftrightarrow \pm 1/2$ transitions than for $1/2 \leftrightarrow -1/2$ transition whose frequency is, only in second order, dependent on the EFG. Hence the T_{2c}/T_{2w} ratio reported in Table II is a qualitative measure of the relative number of B nuclei experiencing the same EFG as the central atom in its neighbourhood or reciprocally, a measure of the difference between the EFG on the central B atom and the average EFG on its B neighbours. Now considering this ratio for the glassy samples, one sees that T_{2c}/T_{2w} is lower than in the crystals. This is expected due to structural disorder. However, the values of this parameter are rather close for a-$Ni_{60}B_{40}$ and c-Ni_4B_3 which indicates a certain coherence of the structure extending further than the first coordination shell. For decreasing B content this ratio decreases confirming the higher disorder or the greater variety of B envirnments for intermediate concentrations. For x = 18.5 it increases slightly again; though there is a great uncertainty on the value of T_{2c}/T_{2w} for this sample, this is consistent with the weaker fluctuations of the B environments.

IV. DISCUSSION

In a-$Ni_{81.5}B_{18.5}$ the narrow distribution of the measured EFG parameter shows that there are only weak fluctuations of the boron coordination (position and nature of the surrounding atoms). The measured value of the asymmetry parameter η in this glass shows that the symmetry of the local charge distributions is the same as in c-Ni_3B. Although we are aware of the fact that the EFG may not be unequivocally related to the local arrangement of the surrounding atoms, these results show that in any case B atoms are not included in a random packed network of Ni atoms and that most probably they are surrounded by the same Ni trigonal prisms as in c-Ni_3B. However boron-boron distances

are larger in the glass than in the crystal due to lower B concentration which means that such prisms would be differently interconnected and hence nickel coordination might be quite different in the two compounds. The higher EFG strength ($\bar{v}_Q$) found in the glass is probably due to medium and long range disorder as explained below.

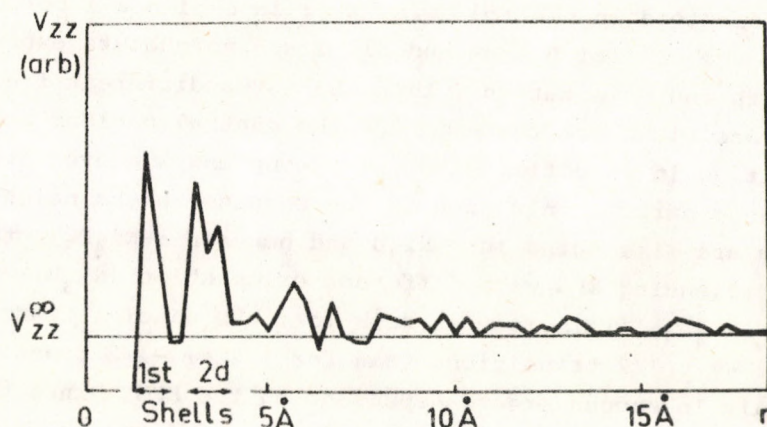On Fig. 10 is shown the EFG strength ($V_{zz}(r)$), computed in a point

Fig. 10.

V_{zz} in c-Ni_3B in a point charge model as function of the distance from central atom up to which the calculation is performed (V_{zz}^∞ = computed up to 40 Å).

charge model (PCM) for c-Ni_3B, due to atoms inside a sphere of radius r around a central B atom. It shows that the V_{zz} due to closer atoms (within one or two atomic distances) is on the average larger by a factor of two than the net V_{zz}^∞ due to all atoms (up to 40 Å). Although PCM does not apply quantitatively to metals, this overshoot of $V_{zz}(r)$ is presumably realistic (which is also found valid for c-Ni_2B and c-Ni_4B_3). It means that in the crystals the contribution of atoms further than a few Å is still important since they considerably reduce the EFG due to the closer ones. On the contrary, in the glasses, the shells of neighbours distant by a few Å from the central atom are certainly much more isotropic (on the average) and their contribution to the mean EFG less important than in crystals (but they will contribute to the EFG fluctuations). As a consequence the net mean EFG in glasses should be determined mostly by the closest neighbours. Recent EFG computations [6] for random network of metal and metalloid spheres show that V_{zz}^∞ is attained within a few percent for a calculation limited to $r \simeq 4$ Å while in the crystal structure $V_{zz}(r)$ is still about 50 % higher than V_{zz}^∞ in that range. This can explain in our case the higher $\bar{v}_Q$ found in the glasses with respect to the corresponding crystals. Similarly, for a-$Ni_{60}B_{40}$, the results show that the boron environments resemble closely those in c-Ni_4B_3. Furthermore the results for $T_2's$ can be interpreted as a trend for the trigonal prisms to pack in a

similar way as in this crystall, i.e. to share rectangular faces allowing B-B
bondings which is consistent with the brittleness of the samples with high
B content.

For the intermediate concentration range ($25 \leq x \leq 35$), the situation
is less clear. Actually we cannot exclude the possibility of random packed
structures, particularly around $x = 31$. But the distribution of ν_Q's is still
narrower than that for a RPN and in our opinion the higher degree of disorder
in these samples results from a mixture of c-Ni_3B-like (a-$Ni_{81.5}B_{18.5}$) and
c-Ni_4B_3-like (a-$Ni_{60}B_{40}$) structures at the atomic scale. Indeed this would
result in ν_Q's ranging from 200 kHz to 300 kHz and η's from 0.2 to 0.6. This
gives an η distribution comparable to that computed for a RPN (Fig. 11)
except the absence of high η's which results in spectra slightly flatter
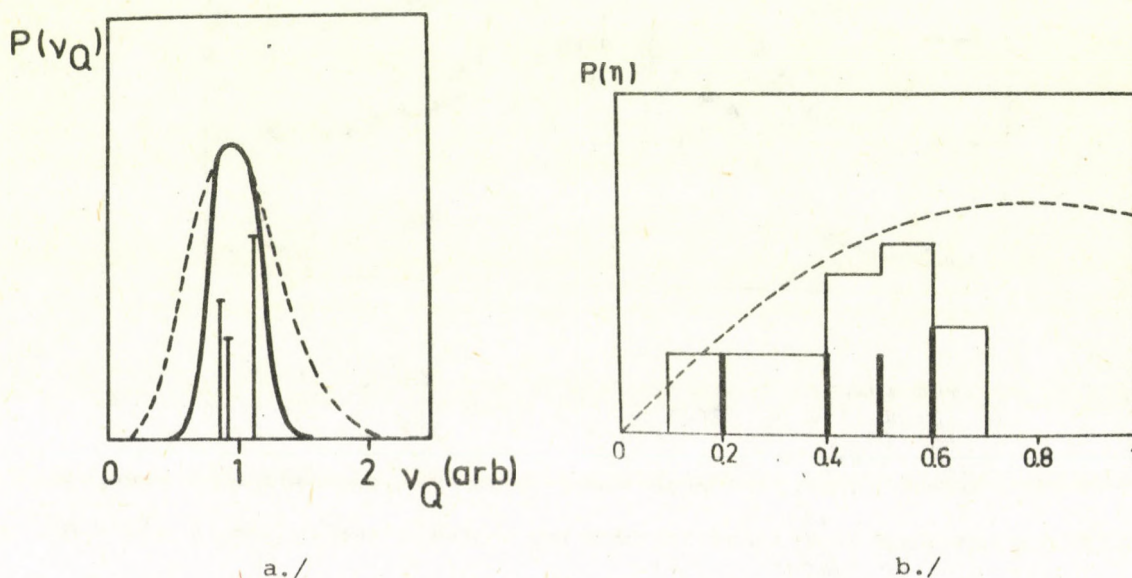

a./   b./

Fig. 11.

ν_Q (a) and η (b) marginal distributions computed for a random
packed network (after Czjzek [1]) (dashed line) and corresponding
distributions for $x = 31$ assuming a mixture of c-Ni_3B-like and
c-Ni_4B_3-like environments (relative weight deduced from fit).

close to the central line than that for the RPN. However, this description
of the glass structure in terms of c-Ni_3B-like basic cells would imply that
boron atoms have no B or two B nearest neighbours only, in which case sites
with two boron neighbours would form long coherent zigzag chains. Though the
present experiments suggest a tendency to such coherence in a-$Ni_{60}B_{40}$, it is
certain that such chains are quite limited in lengths, and that there are
also sites with only one B neighbour (i.e. pairs of Ni prisms sharing 4 Ni),
non existent in the crystalline structures.

Finally no sign of an axial boron environment similar to the Ni anticubes
in c-Ni_2B is observed in the glasses. Actually it has been found [8] that one
crystallization product of the amorphous samples is a metastable Ni_7B_3 phase

(x = 30) in which B is again at the center of Ni trigonal prisms. This result is quite different of the one previously obtained for a-$Mo_{70}B_{30}$ [4] where axial symmetry of the B environment was observed as in c-Mo_2B (tetragonal I_4/mcm as Ni_2B) (Fig. 12). It is worth noticing that the EFG in a-$Mo_{70}B_{30}$
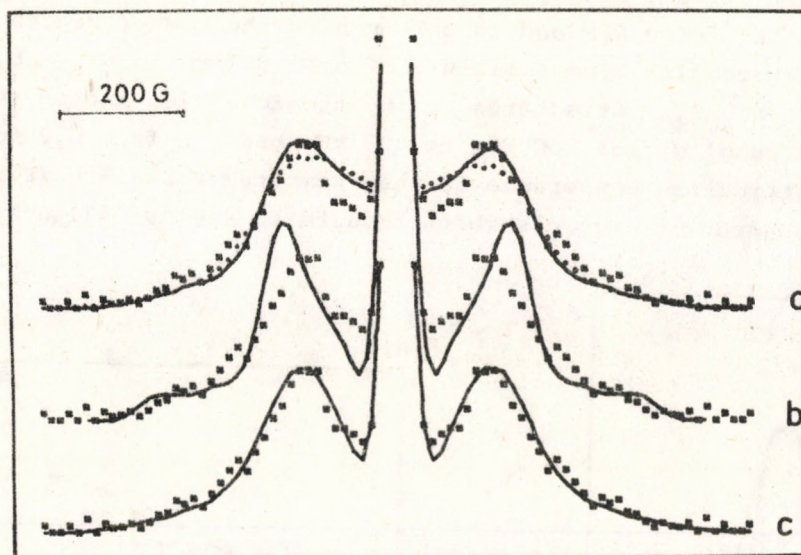

Fig. 12. B experimental spectrum in a-$Mo_{70}B_{30}$ (crosses). Full line:
(a) Simulated spectrum for $\bar{\nu}_Q = 420$ kHz, $\eta = 0$, $\sigma/\bar{\nu}_Q = 0.2$.
(Dots: id. except $\eta = 0$ and $\sigma/\bar{\nu}_Q = 0.25$ or $\eta = 0.2$ and $\sigma/\bar{\nu}_Q = 0.2$).
(b) B experimental spectrum in c-Mo_2B compressed 10 % along the horizontal axis.
(c) Same as (b) except 20 % rms width distribution of the compression factor is added.

($\bar{\nu}_Q = 420 \pm 40$ kHz) [9] is close to (even slightly lower than) that in c-Mo_2B ($\nu_Q = 480 \pm 20$ kHz) in contrast with the case of the Ni-B system; this is consistent with the higher symmetry which certainly implies a larger coherence length of the local structure and hence a smaller difference of V_{zz} in the crystal and in the glass. Such a difference between the structures of $Mo_{70}B_{30}$ and $Ni_{67}B_{33}$ glasses might be related to the fact that Mo_2B is the only stable molybdenum boride phase is that concentration range.

V. CONCLUSION
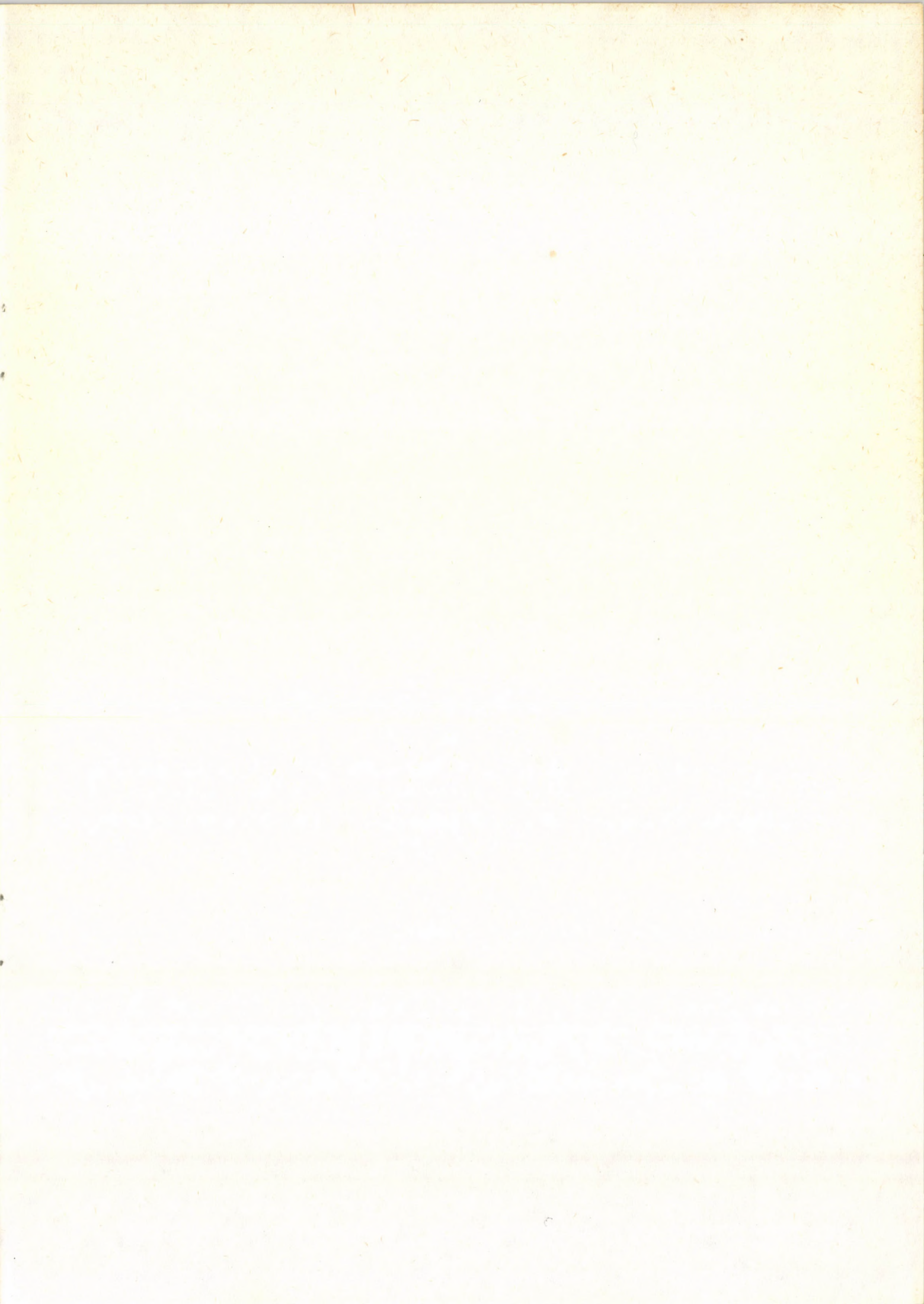
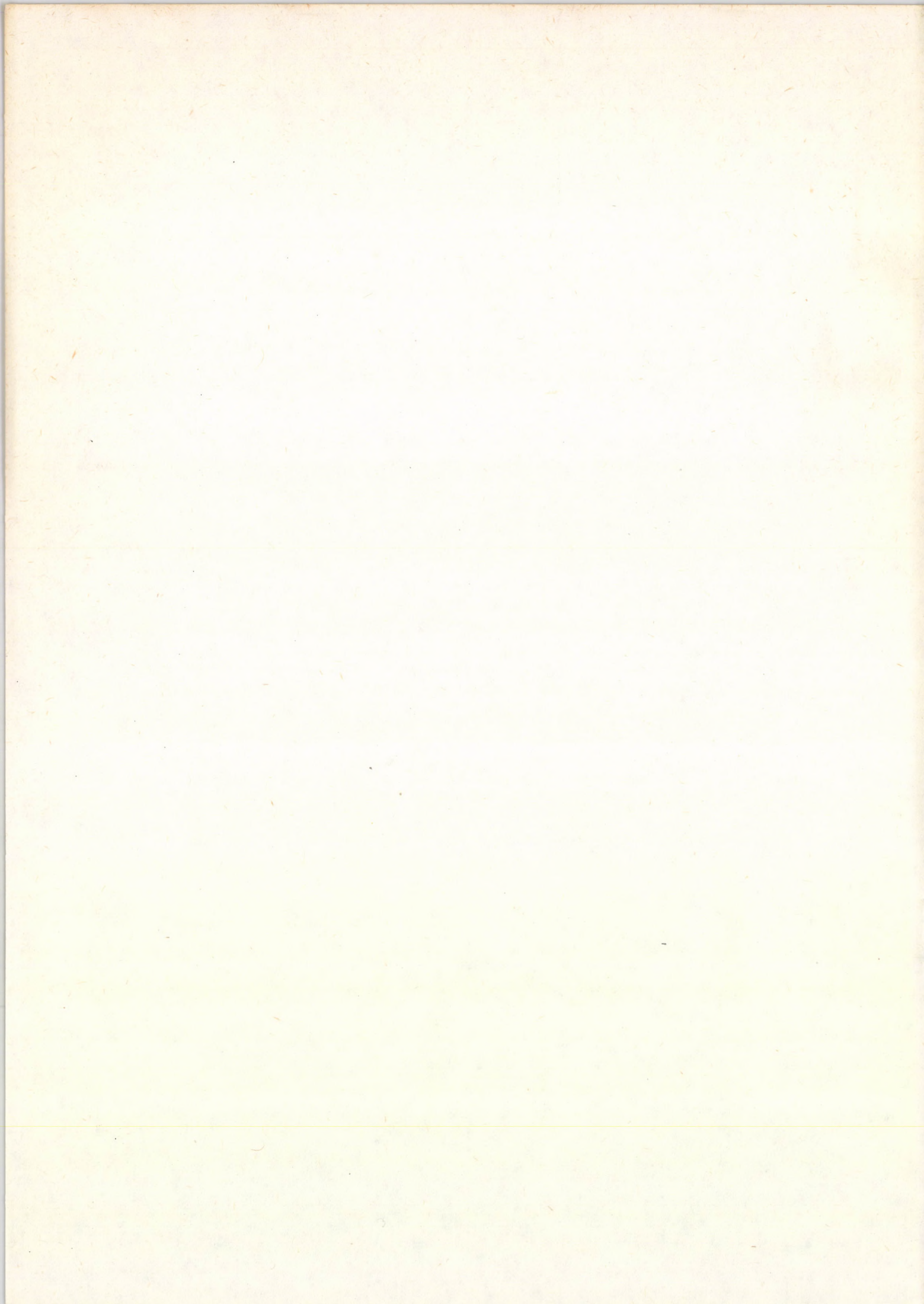This NMR study of the electric field gradient around boron in a-$Ni_{100-x}B_x$ glasses shows that for the eutectic composition (x ≈ 18.5) the boron coordination is rather well defined, i.e. the number, nature and position of the surrounding atoms fluctuate from site to site much less than in a random packed network. Furthermore the symmetry of the boron environment is the same
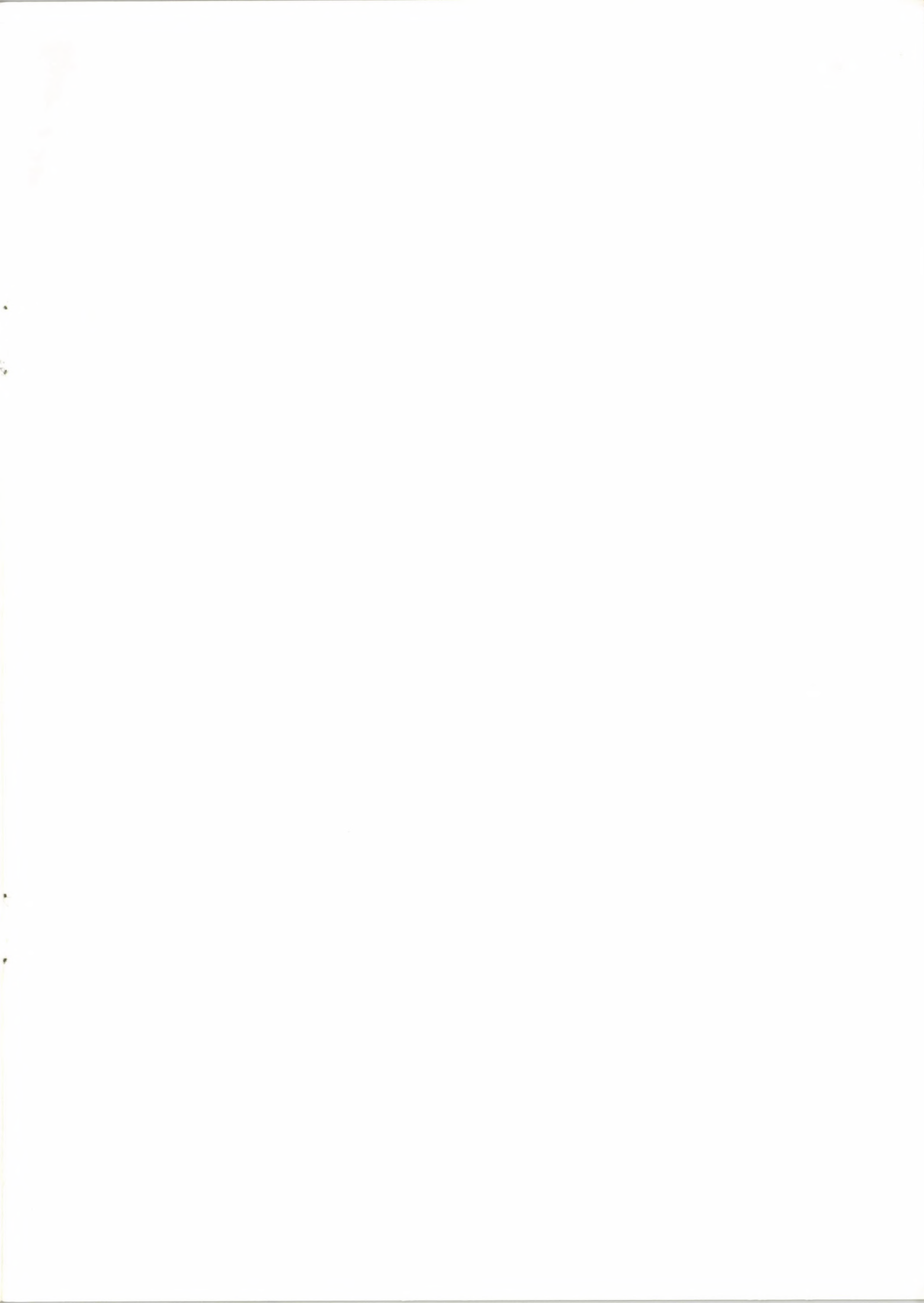
as in c-Ni_3B. It is then concluded that boron is surrounded by nickel trigonal prisms as in most nickel borides, excluding Ni_2B. When boron concentration increases, the degree of fluctuations or the variety of B environment increases as revealed by a broader distribution of the EFG. This variety, however, differs from that expected from random packing since environments with strong asymmetry are absent. Indeed for the highest available boron concentration ($x = 40$), our results can be quite satisfactorily interpreted if boron environments are trigonal prisms similar to those in c-Ni_4B_3. No axial symmetry corresponding to nickel anticubes as in c-Ni_2B is observed in the glasses but rather there is a continuous variation of the average EFG strength and symmetry with varying B content. It is also suggested that in all glassy nickel borides B is surrounded by 6 Ni atoms arranged on trigonal prisms randomly packed as suggested by Gaskell [10]. To accomodate the increasing boron concentration these prisms would share more Ni atoms with other prisms, ultimately sharing rectangular faces allowing B-B contacts in the high boron concentration region.

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[9] In Ref. 4, the scale on Fig. 2 is 200 G instead of 100 G. Due to this scaling error, values for $\bar{\nu}_Q$ in c-Mo_2B, a-$Mo_{70}B_{30}$ and a-$Mo_{42}Ru_{38}B_{20}$ stated in Table I are half the actual ones.

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[11] Note: experimental spectra have been made symmetric in order to improve the signal-noise ratio and the accuracy of the determination of the EFG parameters.

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