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ORDER IN METALLIC GLASSES

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АННОТАЦИЯ

Ближний порядок металлических стекол $(\text{Fe}, \text{Ni})\text{B}$, полученных быстрым охлаждением расплава, очень похож на порядок аналогичного кристаллического материала Fe_3B : тетрагональный, Ni_3B : орторомбический/. В области большой концентрации атомов Ni распределение атомов переходных металлов не случайное. Атомы Ni чаще попадают на места, соседствующие с большим числом атомов бора.

KIVONAT

Olvadék gyorshűtésével előállított $(\text{Fe}, \text{Ni})\text{B}$ üvegek rövidtávu rendje igen hasonló a megfelelő kristályos anyagéhoz (Fe_3B : tetragonális, Ni_3B : ortorombos). Az átmeneti fématomok eloszlása nem véletlenszerű a Ni-dus összetétel-tartományban; a Ni atomok nagyobb gyakorisággal kerülnek a több B szomszédal rendelkező helyekre.

ABSTRACT

The atomic arrangement in melt-quenched (Fe,Ni)B glasses closely resembles that of the crystalline counterparts (Fe_3B is tetragonal, Ni_3B is orthorhombic). The distribution of transition metal atoms is not random at high Ni concentrations: Ni atoms prefer a neighbourhood with a higher boron coordination.

In the study of chemical short-range order Mössbauer spectroscopy is very useful because of its sensitivity to nearest-neighbour environments. Two types of information can be obtained from Mössbauer experiments: 1. the iron hyperfine field is proportional to the iron magnetic moment in transition metal-metalloid glasses and it is determined [1] mainly by the number of nearest metalloid neighbours. Thus the hyperfine field distribution gives the distribution of the local metalloid coordination number around iron atoms. 2. the geometrical arrangement of metalloid neighbours is reflected in the quadrupole interaction.

It has been shown [2] that in the melt-quenched stoichiometric $(\text{Fe,Ni})_3\text{B}$ glasses both the iron hyperfine field and quadrupole splitting closely follow those of the crystalline counterparts indicating that the local symmetry in the amorphous and crystalline structure is similar and changing with Ni substitution. The metastable tetragonal Fe_3B compound formed during crystallization is [3] isostructural to Fe_3P and has three crystallographically inequivalent iron sites in equal numbers with 2B, 3B and 4B nearest neighbours. For the substitution of Ni the

tetragonal structure transforms [4] into the orthorhombic structure of Ni_3B (Co_3B). This cementite type of crystal contains two crystallographically inequivalent Ni sites with 2B and 3B nearest neighbours in a 1:2 ratio. The differences in the environments are clearly reflected in the Mössbauer spectra of Fig. 1. The difference in the atomic arrangements of the tetragonal and orthorhombic unit cells is also reflected in the densities.

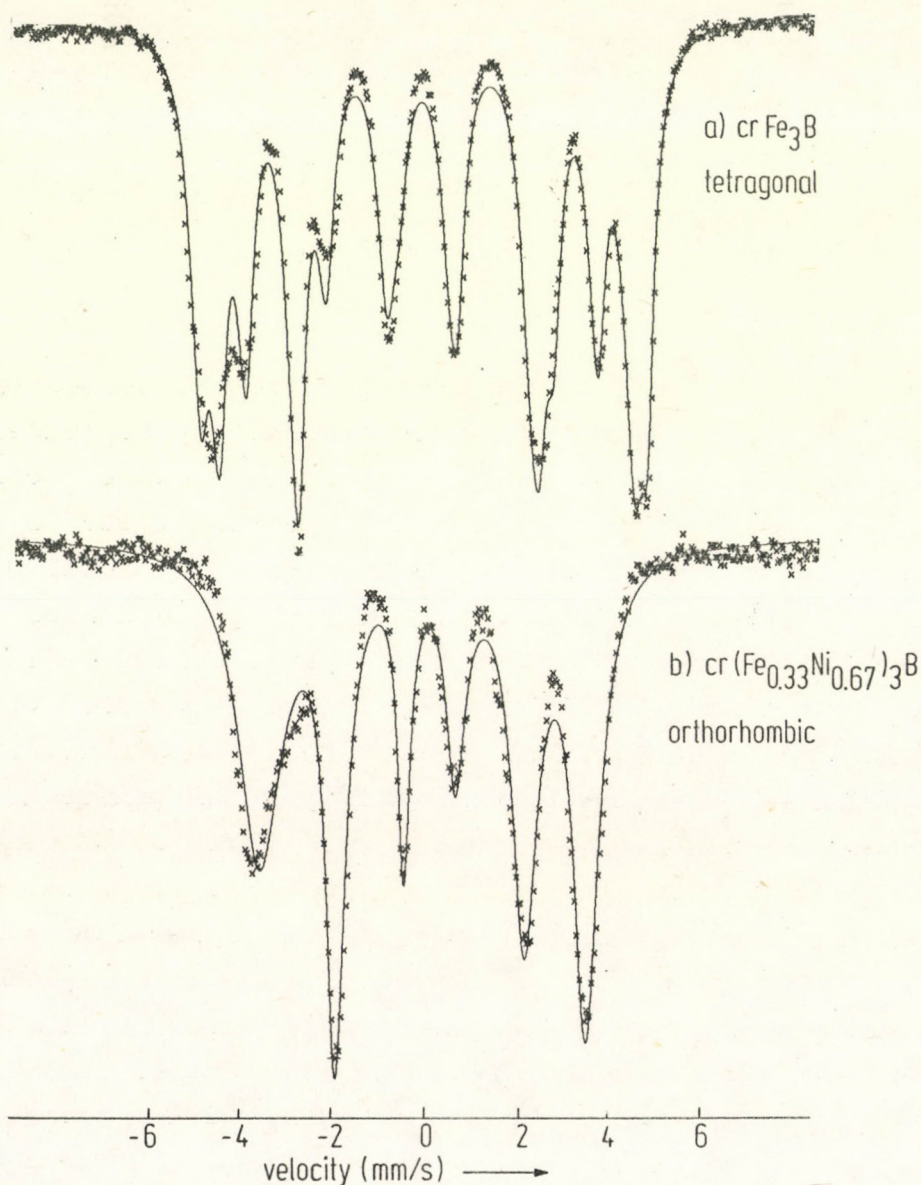


Fig. 1. Mössbauer spectra of crystalline Fe_3B (tetragonal) and $(\text{Fe}_{0.33}\text{Ni}_{0.67})_3\text{B}$ (orthorhombic) at 5 K. The continuous line is the fitted curve

The orthorhombic structure is more densely packed: only half of the observed 10% increase in the density of Ni_3B compared to Fe_3B can be explained by the atomic weight differences. Fig. 2 shows that the density of $(\text{Fe,Ni})_{80}\text{B}_{20}$ glasses [5] follows this trend.

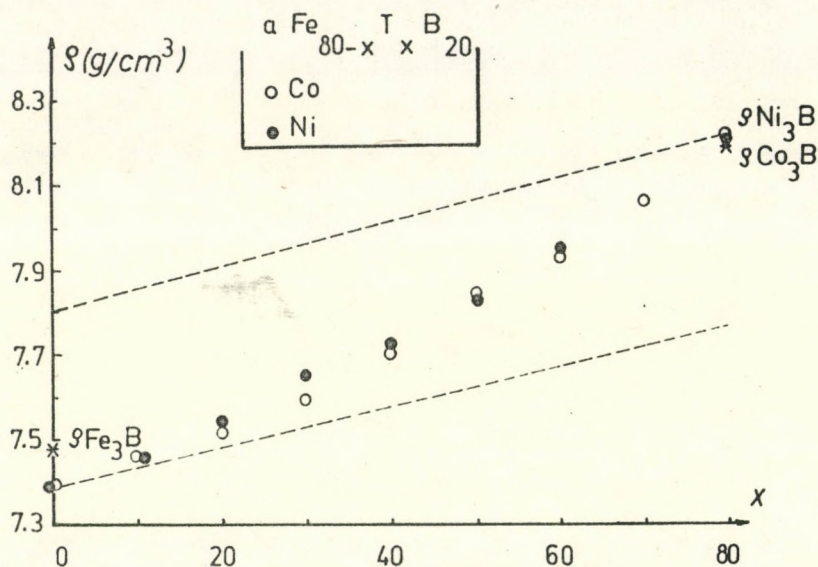


Fig. 2. Densities of amorphous $\text{Fe}_{80-x}\text{T}_x\text{B}_{20}$ ($\text{T} = \text{Co}$ and Ni) alloys taken from Ref. 5. The dashed lines correspond to simple atomic weight differences assuming the packing of $\text{Fe}_{80}\text{B}_{20}$ or $\text{T}_{80}\text{B}_{20}$, respectively. The densities of crystalline Fe_3B , Co_3B and Ni_3B are also shown.

Another manifestation of the change in the local environments of $(\text{Fe,Ni})\text{B}$ glasses is the B concentration dependence of the Curie temperatures (Fig. 3). The T_C cannot be measured in the

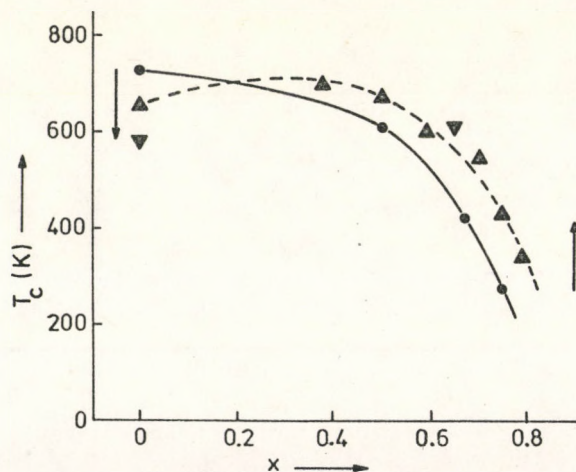


Fig. 3. Curie temperatures of amorphous $(\text{Fe}_{1-x}\text{Ni}_x)_{75+y}\text{B}_{25-y}$ alloys measured by Mössbauer and DSC methods ($y = 0$, $y = 5$, $y = 10$).

whole concentration range because crystallization occurs at lower temperatures. However, it is clear from Fig. 3 that T_c decreases on the Fe-rich side with decreasing B concentration while the opposite is valid for the Ni-rich side. These opposite trends indicate the different electron structure of these glasses due to the different atomic structure.

The change in the topological arrangement at the Fe by Ni substitution can be seen easily in the fine structure of the Mössbauer spectra (Fig. 4). The second line is always narrower

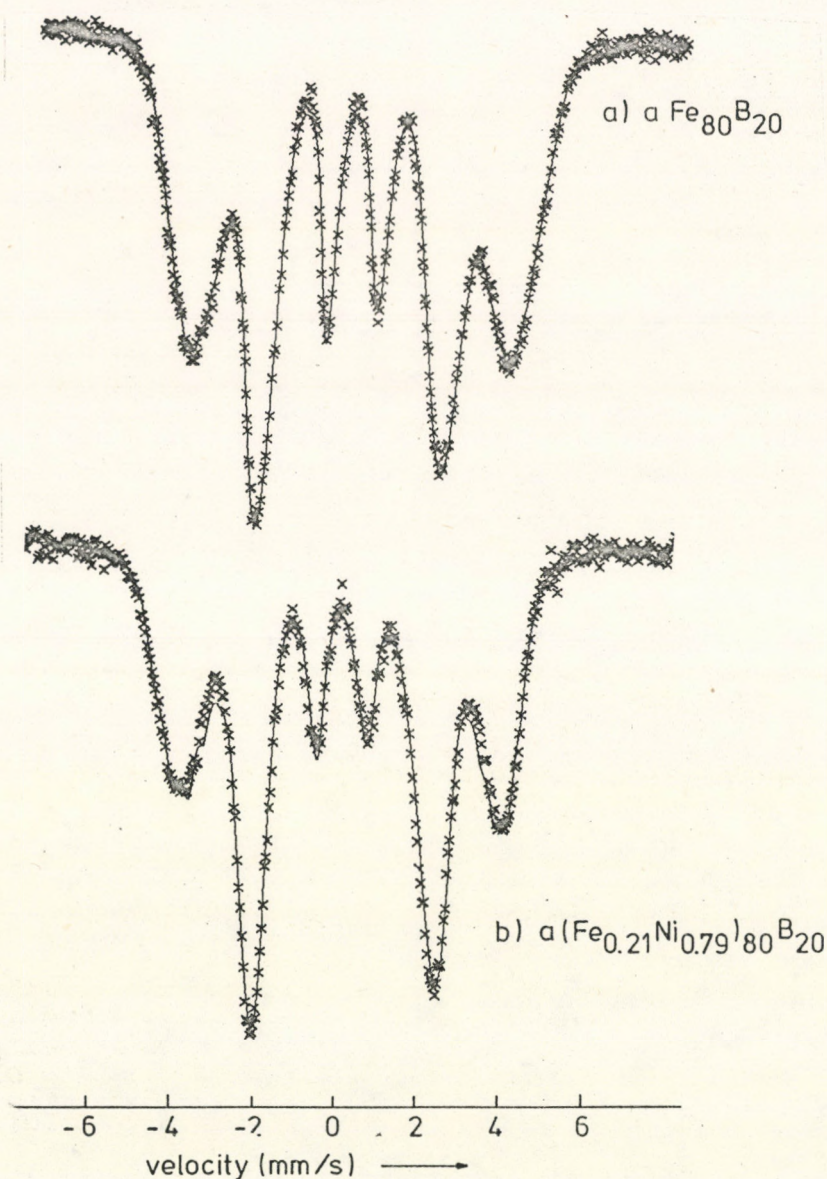


Fig. 4. Typical Mössbauer spectra of amorphous $(\text{Fe,Ni})_{80}\text{B}_{20}$ measured at 5 K

than the fifth line (numbering is from left to right) but in the case of $\text{Fe}_{80}\text{B}_{20}$ the width of the lines 1 and 6 is about equal ($\Gamma_1 \approx \Gamma_6$) while $\Gamma_1 > \Gamma_6$ was found on the Ni-rich side. The former is a result of the compensation of the correlated isomer shift and quadrupole shift distribution (all of them - including the hyperfine field - are determined by the different metalloid configurations). In the case of Ni based glasses the quadrupole interaction is about 50% stronger [2] due to the different local surroundings which overcompensates the effect of isomer shift and results in $\Gamma_1 > \Gamma_6$ and $\Gamma_2 < \Gamma_5$ (the quadrupole interactions influence the lines 1,6 and 2,5 in opposite ways). It is worthwhile to emphasize that this type of asymmetry is characteristic for environments occurring in the orthorhombic structure as it can be seen from the Mössbauer spectrum of the crystalline material shown in Fig. 1b.

The distribution of iron atoms in different local environments is given by the hyperfine field distribution, $p(H)$. The narrowing of this distribution corresponds to a sharper, more "ordered" distribution of iron atoms. Fig. 5 and 6 show that in the B_{20} and B_{15} off-stoichiometric glasses the distribution of Fe environments is narrower for higher Ni concentrations. In the

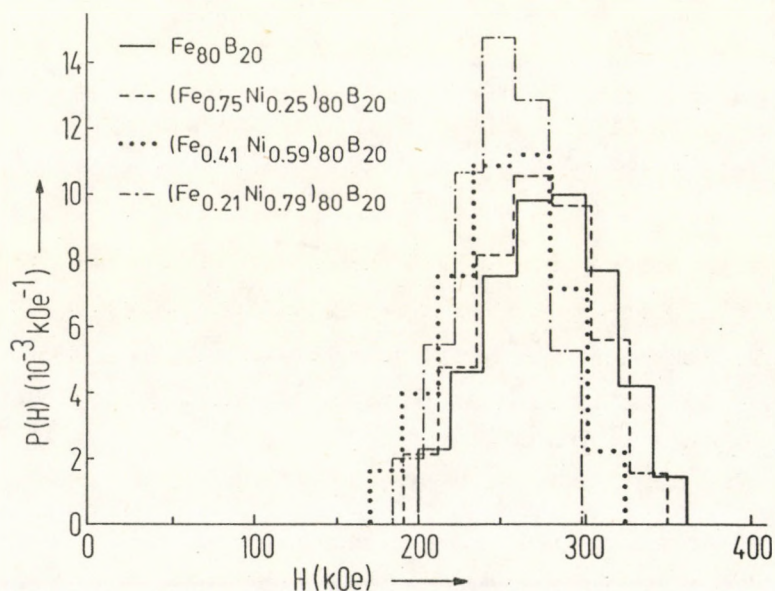


Fig. 5. Typical iron hyperfine field distributions of amorphous $(\text{Fe,Ni})_{80}\text{B}_{20}$ measured at 5 K

case of $(\text{Fe,Ni})_3\text{B}$ glasses the standard deviation of the iron hyperfine field distribution, σ_H is constant. (This apparent concentration independence is due to compensating concentration dependences [4] of the iron hyperfine field with different number of B neighbours as the constancy of σ_H for the different crystal structures shows). As a result of this comparison we had to conclude that the narrowing of $p(H)$ is caused by the increasing number of iron atoms mostly on off-stoichiometric crystallographic sites, which are not present in $(\text{Fe,Ni})_3\text{B}$. This is the first direct evidence that the distribution of transition metal atoms is not random at high Ni concentrations in $(\text{Fe,Ni})\text{B}$ glasses: the Fe atoms prefer less B neighbours than the Ni atoms. The presence of stronger Ni-B than Fe-B interaction is also suggested by recent simple cluster calculation of Messmer [6].

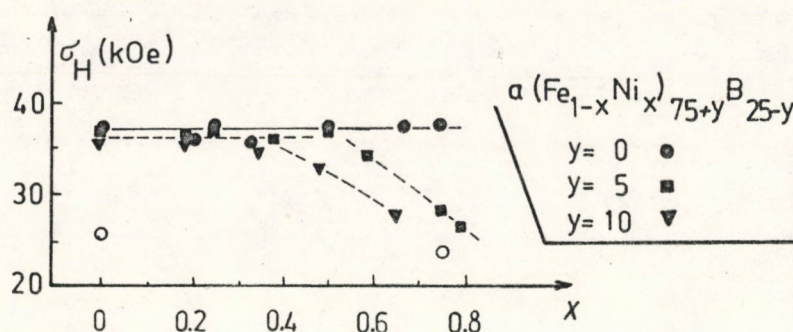


Fig. 6. Standard deviation of the iron hyperfine distributions in amorphous $(\text{Fe}_{1-x}\text{Ni}_x)_{75+y}\text{B}_{25-y}$ measured at 5 K. Empty circles stand for crystalline $(\text{Fe,Ni})_3\text{B}$ compounds.

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