

Correlation between the hyperfine-parameter distributions determined by ^{57}Fe Mössbauer spectroscopy

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The correlations between the hyperfine-field, isomer-shift, and quadrupole-splitting distributions determined in ferromagnetic crystalline and amorphous intermetallic compounds from the linewidth differences of ^{57}Fe Mössbauer spectra will be discussed. It will be shown that no structural information can be deduced from these quantities.

Generally, in iron-containing magnetic crystalline and amorphous materials the low-temperature ^{57}Fe Mössbauer spectrum consists of six broadened peaks. The line broadening results from the variation of hyperfine field H , isomer shift δ , and electric field gradient (EFG) at different iron nuclear sites; correlation between these parameters leads to linewidth asymmetries. It has been shown in a series of papers¹⁻⁶ that the correlation between the width of the distribution of these parameters can be determined from the linewidth differences. By using the notation of Lines and Eibschütz³ the difference in the corresponding mean-square widths $W_i^2 = \langle (L_i - \langle L_i \rangle)^2 \rangle$ [where L_i ($i=1,2,\dots,6$) are the line positions in order of increasing energy] are given by Eq. (5) of Ref. 3 as follows:

$$\begin{aligned} W_6^2 - W_1^2 &= 0.9792\mu_N [\langle \Delta H \Delta \delta \rangle + \langle \Delta H \Delta u \rangle], \\ W_5^2 - W_2^2 &= 0.5672\mu_N [\langle \Delta H \Delta \delta \rangle - \langle \Delta H \Delta u \rangle], \\ W_4^2 - W_3^2 &= 0.1552\mu_N [\langle \Delta H \Delta \delta \rangle - \langle \Delta H \Delta u \rangle], \end{aligned} \quad (1)$$

in which μ_N is the nuclear magneton, u is the first-order quadrupole shift, and $\Delta x \equiv x - \langle x \rangle$ ($x=H, \delta, u$) denotes fluctuations from the average values. Here correlation terms involving the second-order quadrupole shifts which are rather small were neglected. The determination of these linewidth differences by using different fitting procedures was discussed in detail in Refs. 2-6, and our results are in good agreement with the values obtained there. In the following we will investigate the correlations between the fluctuations of the hyperfine parameters in crystalline and amorphous transition metal-metalloid alloys.

$$\langle \Delta H \Delta \delta \rangle$$

The hyperfine field has isotropic and anisotropic contributions. The dominant contribution is isotropic and determined mostly by the number of nearest-neighbor

metalloid atoms via the magnetic moment of the iron atom.⁷ This contribution is not sensitive for the geometrical arrangement of the metalloid neighbors. The anisotropic contributions originate from the antishielded orbital and dipole fields. They depend on the actual geometrical positions of the neighboring atoms, and in the case of uniaxial magnetic anisotropy the electric field gradient is expected⁸ to be proportional to the dipolar field according to the relation $H^d = \mu_B q (1-R)^{-1}$, where μ_B is the Bohr magneton, q is the principal EFG component, and R is the Sternheimer shielding factor. The value of the isomer shift is mainly determined by the number of the metalloid neighbors. In case of crystalline compounds the average values of the hyperfine field and isomer shift are to a good approximation linearly correlated to each other, with $d\bar{H}/d\bar{\delta} \cong -20$.⁹ This relation is well followed also by the average values of transition metal-metalloid glasses.

In the following we will use a similar decomposition for the width of the hyperfine field distribution ΔH , that is $\Delta H = \Delta H^{\text{is}} + \Delta H^{\text{anis}}$, where ΔH^{is} and ΔH^{anis} are the widths of the isotropic and anisotropic hyperfine field distributions, respectively. ΔH^{anis} will not be correlated to $\Delta \delta$, because the isomer shift is independent of the neighbor geometry, so that ΔH^{anis} would average out, i.e., $\langle \Delta H^{\text{anis}} \Delta \delta \rangle \approx 0$. Assuming that the correlation between the widths of the hyperfine field and isomer shift distributions follow the correlation between the average values, the value of $\langle \Delta H \Delta \delta \rangle$ is given by

$$\langle \Delta H \Delta \delta \rangle \cong \langle \Delta H^{\text{is}} \Delta \delta \rangle \cong (d\bar{H}/d\bar{\delta}) \langle (\Delta \delta)^2 \rangle. \quad (2)$$

This relationship is well followed, e.g., by the data deduced for the tetragonal $\text{Fe}_3\text{B}_{1-x}\text{P}_x$ compounds shown in Fig. 1.

However, the value of $\langle \Delta H \Delta \delta \rangle$ is not characteristic for the crystal structure of the compound. For example, in the case of crystalline compounds with single crystallographic sites (e.g., tetragonal Fe_2B , where $\Delta \delta \equiv 0$)¹² or in the materials, where the effect of the increasing number of

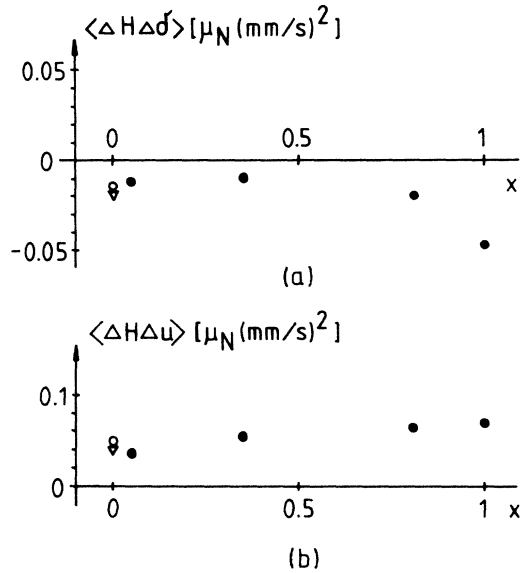


FIG. 1. (a) $\langle \Delta H \Delta \delta \rangle$ and (b) $\langle \Delta H \Delta u \rangle$ correlations in tetragonal $Fe_3B_{1-x}P_x$ compounds calculated from the data of Ref. 11, \bullet ; Ref. 10, ∇ ; and our data, \circ ; respectively.

metalloid nearest neighbors and the decreasing interatomic distances accidentally cancel each other (as is the case of orthorhombic Fe_3C where $\Delta\delta \approx 0$),¹³ the value of $\langle \Delta H \Delta \delta \rangle$ is nearly vanishing, as shown in Table I. Beside that, rather similar values are obtained for the tetragonal Fe_3B and for the Ni-rich orthorhombic $(Fe_{0.33}Ni_{0.67})_3B$ compound, which is¹⁴ isostructural with Fe_3C (Table I), showing that the $\langle \Delta H \Delta \delta \rangle$ correlation is independent of the actual crystal structure or the local geometrical arrangement of the atoms. It is even more surprising that the negative value of $\langle \Delta H \Delta \delta \rangle$ changes for positive values with increasing iron concentration in the orthorhombic $(Fe_{1-x}Ni_x)_3B$ compounds (Table I). The relevant Mössbauer spectra are shown in Fig. 2. It is obvious from the comparison of Figs. 2(c) and 2(d) that the change in the sign of the $\langle \Delta H \Delta \delta \rangle$ correlation in the orthorhombic $(Fe_{1-x}Ni_x)_3B$ compounds for $x=0.67$ and 0.33 originates from the reversion of the relation between the hyperfine fields and isomer shifts of the 2B and 3B sites. At $x=0.67$ the component with the smaller hyperfine field (belonging to the sites with 3B nearest neighbors) has larger isomer shift than the component belonging to the 2B sites; i.e., it follows the trend of the average

values. On the other hand, at $x=0.33$ the larger hyperfine field component has the large isomer shift. (The intensity differences of these components are related to the ordering of the Fe atoms on the 2B sites for increasing Ni concentration.) This latter behavior is also observed^{10,11} in the tetragonal Fe_3B and Fe_3P compounds: The isomer shift of 3B sites is smaller than that of the 2B sites, while the hyperfine field decreases monotonously with increasing number of metalloid neighbors. The negative $\langle \Delta H \Delta \delta \rangle$ correlation in these latter compounds results from the compensation of the negative contribution of the 4B sites, which is, however, absent in the orthorhombic structure. The surprising composition dependence observed in the orthorhombic $(Fe_{1-x}Ni_x)_3B$ compounds is probably related to the concentration dependence of the atomic position parameters in the structure, that is, to the change of the interatomic distances.¹⁴ However, at present no direct experimental information is available.

In most metallic glasses (apart from the Fe-P glasses) the $\langle \Delta H \Delta \delta \rangle$ correlation does not have³⁻⁶ the negative value expected on the base of the correlation between the average values. A typical value of $\mu_N \langle \Delta H \Delta \delta \rangle$ is $+0.029 (\text{mm/s})^2$ for amorphous $Fe_{76}B_{24}$ alloy.³ However, in the case of amorphous alloys, there is a further contribution to the correlation of $\langle \Delta H \Delta \delta \rangle$, which is not present in the crystalline compounds and which originates from the fluctuations of the interatomic distances around the average values via the interatomic distance dependence of $H(r)$ and $\delta(r)$. The estimated value of this contribution is the following:

$$\begin{aligned} \langle \Delta H(r) \Delta \delta(r) \rangle &\simeq \frac{d\bar{H}}{dr} \frac{d\bar{\delta}}{dr} \langle (\Delta r)^2 \rangle \\ &= \frac{d\bar{H}}{dp} \frac{d\bar{\delta}}{dp} \left(\frac{dp}{dr} \right)^2 \langle (\Delta r)^2 \rangle \\ &= 9 \frac{d\bar{H}}{dp} \frac{d\bar{\delta}}{dp} \frac{1}{K^2} \langle (\Delta r/r)^2 \rangle, \end{aligned} \quad (3)$$

where it was assumed that it follows the correlation between the average values. Here $\langle (\Delta r/r)^2 \rangle^{1/2}$ is the relative fluctuation of transition metal-metalloid interatomic distances, and $K = -d \ln V / dp$ is the compressibility. The distance dependence of the hyperfine field and the isomer shift is in this way rescaled to their pressure dependence. High-pressure Mössbauer study of amorphous Fe_3B and $(Fe_{0.25}Ni_{0.75})_3B$ gives¹⁵ the following typical values: $d\bar{H}/dp = -0.2 \text{ kOe/kbar}$ and $d\bar{\delta}/dp$

TABLE I. Values of the $\langle \Delta H \Delta \delta \rangle$ and $\langle \Delta H \Delta u \rangle$ correlations in different intermetallic compounds (error bars are given in parentheses).

	Crystal structure	$\langle \Delta H \Delta \delta \rangle$	$\langle \Delta H \Delta u \rangle$	Crystal structure	$\langle \Delta H \Delta \delta \rangle$	$\langle \Delta H \Delta u \rangle$
		μ_N (mm/s) ²	μ_N (mm/s) ²		μ_N (mm/s) ²	μ_N (mm/s) ²
Fe_2B	Tetragonal	+ 0.0003(10)	+ 0.0129(10)			
Fe_3C	Orthorhombic	+ 0.0038(10)	+ 0.0065(10)			
Fe_3B	Tetragonal	- 0.014(5)	+ 0.050(5)	amorphous	+ 0.028(10)	- 0.039(10)
$(Fe_{0.67}Ni_{0.33})_3B$	Orthorhombic	+ 0.022(5)	- 0.015(5)	amorphous	+ 0.012(10)	- 0.028(10)
$(Fe_{0.33}Ni_{0.67})_3B$	Orthorhombic	- 0.029(5)	- 0.068(5)	amorphous	+ 0.021(10)	- 0.046(10)

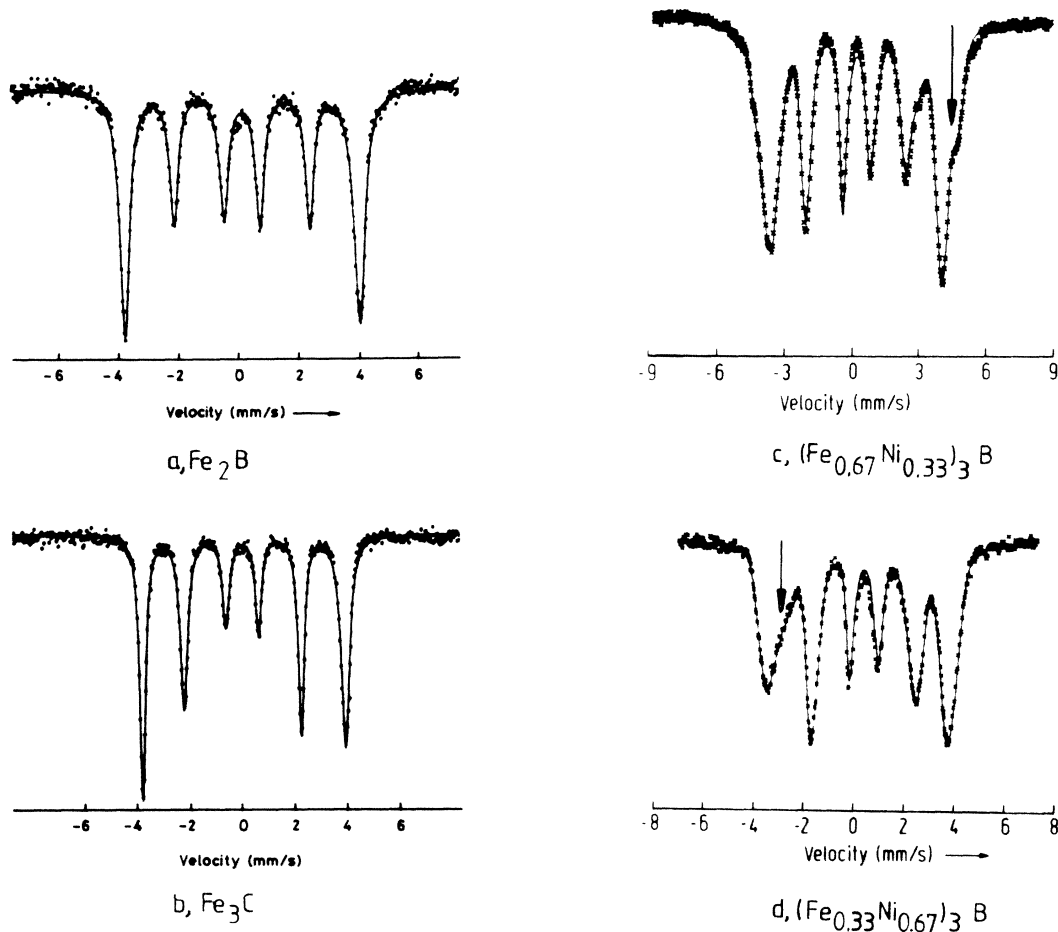


FIG. 2. (a) Mössbauer spectra of tetragonal Fe_2B at 293 K, (b) orthorhombic Fe_3C at 80 K, (c) orthorhombic $(\text{Fe}_{0.67}\text{Ni}_{0.33})_3\text{B}$, and (d) $\text{Fe}_{0.33}\text{Ni}_{0.67})_3\text{B}$ at 5 K. The arrows in (c) and (d) correspond to the satellite with larger hyperfine field and larger isomer shift and to the satellite with smaller hyperfine field and larger isomer shift, respectively.

$= -3 \times 10^{-4} \text{ mm/s kbar}$. $K = 6 \times 10^{-4} \text{ kbar}^{-1}$ can be extrapolated from the measured K values of different Fe and Ni containing metallic glasses.¹⁶ High-resolution time-of-flight neutron diffraction study of Fe-B and (Fe,Ni)B glasses yields¹⁷ $\Delta r/r \approx 0.03$ for the relative Fe-B distances. With these parameters the contribution of the distance fluctuation to $\langle \Delta H \Delta \delta \rangle$ is about $\approx +0.06 \mu_N$ (mm/s)² according to Eq. (3). The characteristic difference⁴ between Fe-B and Fe-P glasses must be caused by the delicate balance of the two main contributions: short-range order and interatomic distance fluctuations.

$$\langle \Delta H \Delta u \rangle$$

By using the formerly adapted decomposition of the hyperfine field into isotropic and anisotropic contributions, correlation is expected only between ΔH^{anis} and Δu . In case of uniaxial magnetic anisotropy $\Delta H^{\text{anis}} \sim \Delta u$, according to the formerly mentioned⁸ relationship between the dipole fields and quadrupole shifts; thus positive $\langle \Delta H \Delta u \rangle$ correlation is expected. This expectation is well fulfilled for the crystalline $\text{Fe}_3\text{B}_{1-x}\text{P}_x$ compounds

(Fig. 1) or for the tetragonal Fe_2B (Table I), where the Mössbauer spectra indicate^{11,12} uniaxial magnetic anisotropy. On the other hand, when this assumption does not hold, as in the case of orthorhombic $(\text{Fe}_{1-x}\text{Ni}_x)_3\text{B}$ compounds where a broad distribution of dipolar fields had to be used for the description of the Mössbauer spectra, negative $\langle \Delta H \Delta u \rangle$ correlations were obtained (Table I). Negative $\langle \Delta H \Delta u \rangle$ correlations were obtained (Table I). Negative $\langle \Delta H \Delta u \rangle$ values are characteristic also for metallic crystalline data they may be caused by their nonaxial magnetic structure.

Finally we had to conclude that the values of the $\langle \Delta H \Delta \delta \rangle$ and $\langle \Delta H \Delta u \rangle$ correlations determined for compounds of known crystalline structure show no simple relation to the local neighborhoods of iron atoms. In this way it is hardly expected that the dominant short-range order of metallic glasses is reliably estimated from these correlations.

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