Averaged spin orientation in amorphous $Fe_{81}B_{19}$ systems under uniaxial compression

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An NGR spectroscopic study is made of the volume-averaged spin orientation of an amorphous $Fe_{81}B_{19}$ ribbon under cyclic uniaxial loading of the sample. In the relieved state of the sample, it is found that the hyperfine field at the Fe nucleus fluctuates depending on the loading history. A qualitative model is proposed which describes the observed character of the behavior of the averaged spin orientation.

1. INTRODUCTION

The study of the behavior of the hyperfine fields in ferromagnetic amorphous alloys under external influences (heat treatment, pressure, strain) has in recent years yielded interesting new results.

Information on the averaged spin orientation in ferromagnets is obtained directly from the relationship of the intensities of the lines of the hyperfine splitting in the experimental Mössbauer spectra.

It has been found[1,2,3] that the amorphous alloys $Fe_{82}B_{12}Si_6$ and $Fe_{40}Ni_{38}Mo_4B_{12}$ at annealing temperatures above 650 K exhibit an increase in the component of the magnetic anisotropy field perpendicular to the surface of the ribbon. Changes in the direction of the averaged spin orientation have also been found to occur under uniaxial extension of amorphous ribbons of the same composition. Therefore, the results of those studies were attributed to the creation of strictional fields by internal strains arising during heat treatment.

An interesting observation made in Refs. 4, 5, and 6 is that fluctuational changes are present in the averaged spin orientation in the amorphous alloys $Fe_{81}B_{19}$ and $Fe_{81}B_{13.5}Si_{3.5}C_2$ during isochronal annealing.

In Ref. 7 it was found that during isothermal annealing within the limits of the amorphous state of Fe–B alloys ($T_{ann} = 520$ K), the dependence of the direction of the averaged spin orientation on the annealing time has a fluctuational character (a reversible rotation of the spins with respect to the plane of the amorphous ribbon was observed as time went on).

In the present study we use the methods of NGR spectroscopy to investigate the nature of the change in the volume-averaged spin orientation in amorphous ribbons of composition $Fe_{81}B_{19}$ under uniaxial extension.

2. EXPERIMENTAL TECHNIQUES

In the experiments we used amorphous samples of the alloy $Fe_{81}B_{19}$ and polycrystalline samples of Armco iron. Amorphous samples of composition $Fe_{81}B_{19}$ were obtained by ultrafast quenching from the melt in the form of ribbons 9–12 mm wide and 25–30 μm thick. The ribbons were fabricated in vacuum on an apparatus with rotating disks. The amorphous character of the samples was established by x-ray diffraction. The samples were ferromagnetic and had a positive saturation magnetostriction ($\lambda = 5\cdot10^{-6}$). The Armco iron samples were rolled to a thickness of 25 μm. The saturation magnetostriction of these samples was negative ($\lambda = -10.7\cdot10^{-6}$). After fabrication, the amorphous and polycrystalline ribbons were subjected to mechanical testing on an Instron 1200 apparatus. The Young's modulus was $5\cdot10^3$ kg/mm^2 for the amorphous $Fe_{81}B_{19}$ ribbons and $1.5\cdot10^4$ kg/mm^2 for the Armco iron samples. Failure of the amorphous samples occurred in the elastic-strain region at $P = 35$ kg/mm^2. With the aid of a differential calorimeter, we determined the crystallization temperature of the amorphous samples and the temperature at which the separate phases precipitated out. The amorphous ribbons were rolled onto a platinum mandrel, through which the contact with the measuring thermocouple was made. The annealing was done in an atmosphere of krypton (the rate of change of the temperature was ≈ 5 °C/min in the range 20–900 °C).

In the experimental apparatus containing the Mössbauer spectrometer, a 500-MBq source of ^{57}Co resonance radiation in an rhodium matrix was set in motion at a constant acceleration. An amorphous (or polycrystalline) ribbon mounted in a holder between the source and detector was periodically subjected to loading in the direction of the longitudinal axis. The Mössbauer spectra of the resonance absorption were measured at a fixed load on the sample and after the load was removed. The lengthening of the sample during loading was determined with the aid of a special comparator equipped with two measuring microscopes. The experimental spectra were measured at room temperature in the elastic-strain region of the loaded samples. To eliminate the influence of stray magnetic fields, the samples were placed in a magnetic shield.

3. RESULTS OF THE MEASUREMENTS

Figure 1 shows the differential temperature dependence of the heat release Q of an amorphous sample of $Fe_{81}B_{19}$. One clearly sees crystallization peaks at $T \approx 440$ °C and 900 °C, the first of which indicates the formation of the metastable Fe_3B phase and the second the formation of the Fe_2B phase and the precipitation of α-Fe (Ref. 8).

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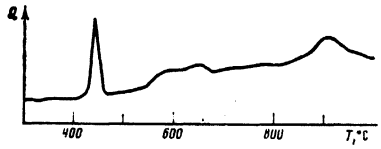

FIG. 1. Differential temperature curve for an $Fe_{81}B_{19}$ sample.

The volume-averaged spin orientation of the sample was determined from the ratios of the intensities I_i of the lines of the hyperfine splitting in the experimental spectra of the resonance absorption of ^{57}Fe (the ratios of the areas under the peaks in the Mössbauer spectra). As we know, these ratios are related to the angle θ between the direction of propagation of the γ rays and the magnetic field at the nucleus in the following way:

$$I_{1,6}:I_{2,5}:I_{3,4}=3:\beta:1, \quad \beta=4\sin^2\theta(1+\cos^2\theta).$$

The experimental Mössbauer spectra were processes on a computer.

Figure 2 shows the ratios of the intensity I_2 of the second line of the Mössbauer absorption spectrum to the intensities I_1 and I_3 of the first and third lines as functions of P during extension of the sample along the ribbon axis. These ratios increase sharply at small loads ($P<1$ kg/mm^2) and reach saturation at $P\approx 10$ kg/mm^2 (the relative lengthening $\Delta l/l$ of the sample at this load is $2\cdot 10^{-3}$ and corresponds to $\Delta l/l$ at a temperature of ~ 200 °C). The experimental dependence $I_2/I_{1,3}=f(P)$ in the region $P<10$ kg/mm^2 has a nonmonotonic character.

When a layer ~ 3 μm thick was electrochemically removed from the contact surface of the sample, the ratio $I_2/I_{1,3}$ in the never-loaded state increased by a factor of 1.5 (Fig. 3), but on loading of the ribbon this ratio reached saturation at the same value as in Fig. 2.

Figure 4 gives the experimental values of the ratio I_2/I_1 obtained in a series of measurements taken on three different samples which were held for a certain time under a load of $P=25$ kg/mm^2, corresponding to saturation of I_2/I_1, then relieved, again loaded, etc. The periods of the cyclic loading of the samples were arbitrarily chosen. The relative lengthening on loading was $5\cdot 10^{-3}$. The change in the spin orientation was averaged over the duration of one measurement of the Mössbauer spectrum, amounting to ~ 100 min. The overall duration of the cyclic change in the external influence on the sample was from 600 to 800 h in different measurements. In all the series of measurements in the loaded state of the samples, the ratio I_2/I_1 was found to be preserved. After the load was removed from the sample, a significant spread of values of this ratio was observed, having a fluctuational character and amounting to 15–20% of the average value (the accuracy with which the ratios $I_2/I_{1,3}$ were determined was 3–4%). In addition, a gradual decrease in the value of I_2/I_1 was observed as the number of loading cycles was increased. These experimental results were obtained on amorphous ribbons of $Fe_{81}B_{19}$ identical to those use din Ref. 4. Analogous results were obtained on $Fe_{81}B_{19}$ samples fabricated on a different apparatus, but they had a smaller scale of fluctuations of I_2/I_1 and are not required here.

Analysis of the results of measurements under an outside influence analogous to that described above but for a polycrystalline sample of Armco iron showed that the ratio I_2/I_1 in this case fluctuates insignificantly in both the loaded and never-loaded states of the sample.[1)] As a control experiment we made lengthy observations of the spin orientation of an $Fe_{81}B_{19}$ sample which was not subjected to cyclic loading. In this case the ratio I_2/I_1 remained constant over 600 h of observations. The control experiment allowed us to rule out possible systematic errors in the measurements and to estimate the accuracy of the experimental results with allowance for the mathematical processing of the Mössbauer spectra.

4. DISCUSSION OF THE RESULTS

Under uniaxial extension of ferromagnetic materials having magnetostriction, the components of the strain tensor and the projections of the magnetization vector are related by[9]

$$U_{zz}=P/E+\lambda M_z^2, \quad U_{xx}=-\sigma P/E+\lambda M_x^2, \quad U_{yy}=-\sigma P/E+\lambda M_y^2, \tag{1}$$

where E is Young's modulus, σ is Poissons's ratio, λ is the magnetostriction constant, P is the force acting per unit cross-section area, and $\mathbf{M}$ is the magnetization vector. It should be noted that the absolute value of the strain is to some extent arbitrary, since the choice of the direction of $\mathbf{M}$ for which the strain is taken to be zero is arbitrary.

As we know, the character of the Mössbauer spectrum

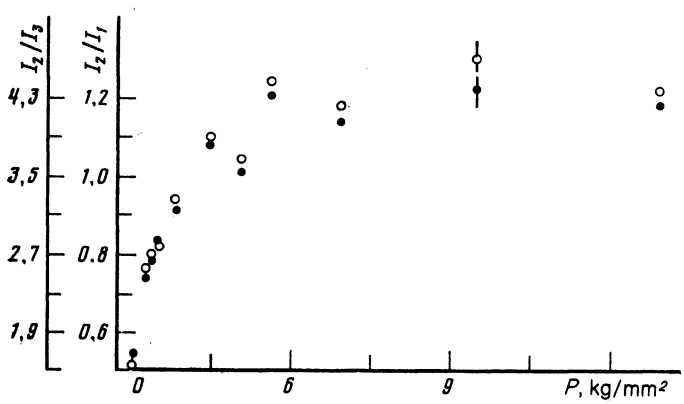

FIG. 2. Experimental dependence of I_2/I_3 (●) and I_2/I_1 (○) on the change in the load P during uniaxial extension of an amorphous sample of $Fe_{81}B_{19}$.

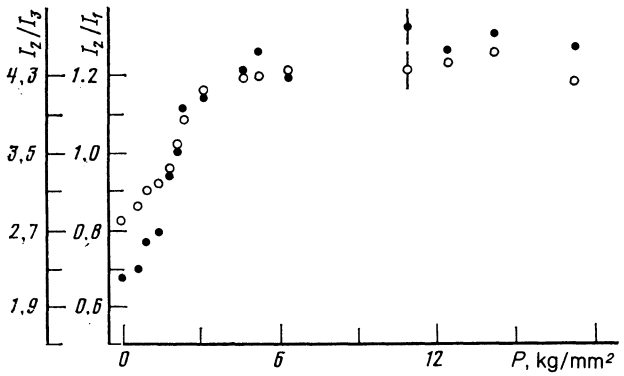

FIG. 3. Experimental dependence of I_2/I_3 (●) and I_2/I_1 (○) on the change in the load P during uniaxial extension of an amorphous $Fe_{81}B_{19}$ sample from which a surface layer 3 μm thick had been removed beforehand by electrochemical means.

depends on the hyperfine field arising at a particular nucleus as a result of the interaction of the nuclear spin with the spin of the individual ion. This field depends on the spin of the individual ion and not on the averaged magnetization, which is a property of the volume as a whole. The hyperfine splitting of the Mössbauer spectrum also reflects indirectly the characteristic properties of the entire system of ion spins, but only to the extent that they determine the temporal characteristics and average orientation of the spin. Thus any changes of the components of the electronic spin S of the atom will immediately lead to a change in the hyperfine field in the case when the characteristic time τ_e for these changes is substantially longer than the period associated with the nuclear frequency ω_L, i.e., for $\omega_L \tau_e \gg 1$ the nucleus reacts to every change in S taken individually, whereas for $\omega_L \tau_e \ll 1$ the nuclear spin feels only the average value of S.

A characteristic feature of the $I_2/I_{1,3}$ dependence in Fig. 2 is that at comparatively small loads ($P \approx 6$ kg/mm^2) the ratio $I_2/I_{1,3}$ tends toward a constant value. This means that a strain as low as $\sim 10^{-3}$ aligns the vector of the hyperfine magnetic field at the nucleus with the plane of the amorphous ribbon. In the transition region ($P < 6$ kg/mm^2) the ratio $I_2/I_{1,3}$ fluctuates about an average value (in the Mössbauer spectra of the Armco iron samples such fluctuations were practically unnoticeable). There fluctuations of the hyperfine field can apparently be attributed to relaxation processes occurring in the magnetostrictive ferromagnetic material as the equilibrium field of the strains is being established at the given load.

The role of relaxation processes is manifested most clearly in the series of measurements whose results are shown in Fig. 4. As we see from the ratio $I_2/I_{1,3}$, the character of the averaged spin orientation of the loaded sample does not change in time, does not depend on the number of load-

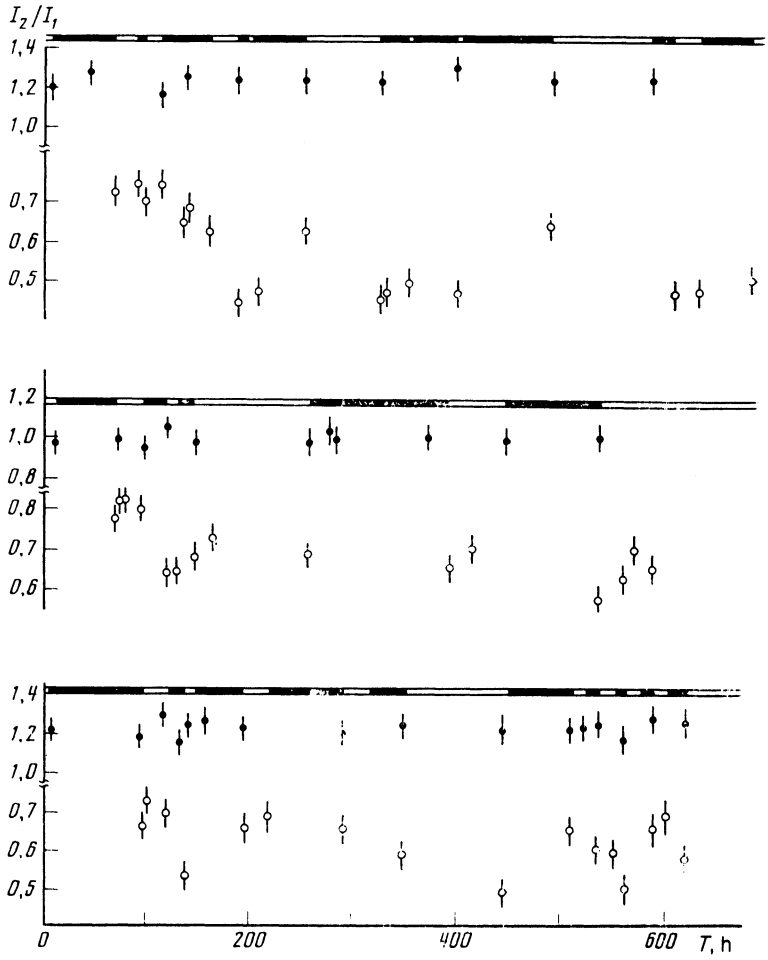

FIG. 4. Experimental values of I_2/I_1 for the loaded (●) and relieved (○) states of three different amorphous samples of $Fe_{81}B_{19}$. The horizontal broken line shows the times during which the sample is loaded (dark segments) and the times when the sample is free (light segments).

ing cycles or their duration, and is described to good accuracy by a straight line. At the same time, the behavior of this ratio during the periods in which the sample is in a relieved state is radically different. It is true for all the series of measurements that in the initial stage of the experiment, after the first loading cycles, the ratio $I_2/I_{1,3}$ is substantially larger in the relieved state than it was before the loading began. In the periods when the sample is in the relieved state, a considerable scatter is observed in the value of $I_2/I_{1,3}$ over time, and the average value of this ratio slowly relaxes to the initial state after many loading cycles. In the control sample of polycrystalline Armco iron the analogous effects were much weaker.

The observed character of the behavior of $I_2/I_{1,3}$ in the amorphous material permits the assertion, first, that the hyperfine field and, with it, the average orientation of the ion spin, fluctuate in the relieved state of the sample, depending on the loading history, and, second, that internal stresses remain in the interior of the amorphous sample after the first loading, giving rise to strictional fields which gradually vanish over prolonged cycling.

Comparison of the result obtained in this study during the uniaxial extension of an amorphous $Fe_{81}B_{19}$ ribbon with the results of studies on the isothermal annealing of a similar sample[7] permits the assumption that the fluctuations of the hyperfine field obtained in the two cases are of a general nature and can be described in the following way on the basis of a qualitative model. Let us assume that the change in the orientation of a spin occurs as a result of an interaction between the given ion and its immediate environment, which changes on account of the jumping of ions into unoccupied sites. For example, for an amorphous Fe–B alloy the spin orientation of a given Fe ion changes if an empty site in its immediate environment becomes occupied as a result of the jumping of another ion, Fe or B. Both the heating of the sample and its straining as a result of an external mechanical influence will give rise to internal stresses that accelerate this process.

The probability of an ion jump-over per unit time is given by the Arrhenius law:

$$v \infty \exp(-U/kT), \tag{2}$$

where T is the temperature and U is the effective potential barrier that must be overcome by the ion.

In contrast to crystalline materials, amorphous materials have a whole spectrum of values of the potential barriers U. In particular, the strains during loading of the sample will give rise to internal stresses and, as a result, to a change in the value and distribution of the effective barriers. The subsequent relieving of the sample entails a new redistribution of the potential barriers and a change in their values, which, in turn, leads to both reversible and irreversible changes of the immediate environment of the given ion because of the jumping of ions and their capture in traps. Therefore, after the load is removed a different distribution of Fe and B ions can arise in the amorphous material because of the change in the spectrum of potential barriers, and for this reason the effective interaction will establish some orientation or other of the spin of the Fe ion. The observed fluctuations of the hyperfine field are evidently due to this circumstance.

An estimate of the fluctuations of the hyperfine field can be made as follows. Suppose that the interaction energy, which determines the averaged orientation of the spins and, with it the macroscopic magnetization **M**, is given by the expression

$$E \sim v_{\mathrm{FeFe}} N_{\mathrm{Fe}} + v_{\mathrm{FeB}} N_{\mathrm{B}}, \tag{3}$$

where v_{FeFe} is the effective interaction of the Fe ion with the Fe ions of the immediate environment of the given ion, v_{FeB} is the interaction of the given Fe ion with the B ions, N_{Fe} is the number of nearest-neighbor iron ions, and N_{B} is the number of nearest-neighbor boron ions.

If the nearest-neighbor configuration changes when the load is removed, then the effective change ΔE in the interaction energy can be written in the form

$$\Delta E \sim v_{\mathrm{FeFe}} \Delta N_{\mathrm{Fe}} + v_{\mathrm{FeB}} \Delta N_{\mathrm{B}}. \tag{4}$$

For estimating the values of ΔN_{Fe} (ΔN_{B}), one can use the well-known relations[10]

$$\overline{(N_{\mathrm{Fe}}{}^2 + \bar{N}_{\mathrm{Fe}}{}^2)}/\bar{N}_{\mathrm{Fe}} = n \int [g(\mathbf{R}) - 1] d\mathbf{R} + 1 + \ldots, \tag{5}$$

where n is the density and $g(\mathbf{R})$ is the radial distribution function. Relation (5) can be expressed in terms of the isothermal compressibility $\varkappa_T$:

$$\overline{N_{\mathrm{Fe}}{}^2} - \bar{N}_{\mathrm{Fe}}{}^2 = \bar{N}_{\mathrm{Fe}} n k T \varkappa_T. \tag{6}$$

Experiments of $(\overline{\Delta N^2})^{1/2}$ using Eqs. (5) and (6) give a value ~ 1, which permits a qualitative explanation of the fluctuations of the hyperfine field observed both during cyclic loading of the sample and during isothermal annealing within the limits of the amorphous state.

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[1)] A comparative experiment with the crystalline analog of $Fe_{81}B_{19}$ cannot be done, since the sample becomes brittle on crystallization.

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