Magnetism and Invar anomaly in the amorphous alloy $Fe_{90}Zr_{10}$

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The magnetism and the nature of the Invar anomaly in the amorphous alloy $Fe_{90}Zr_{10}$ have been investigated. The thermal expansion, saturation magnetization, hysteresis loop and also the Mössbauer spectra of ^{57}Fe nuclei have been measured on one and the same specimens. The experimental results show that the immediate surroundings determine the magnetism of the iron atoms. The Invar anomaly in the amorphous alloy is due to competing ferromagnetic and antiferromagnetic interactions which arise as a result of fluctuations in the interatomic spacings.

1. INTRODUCTION

Amorphous magnetic materials have now been studied intensively for more than ten years. While at first most attention was paid to the amorphous structure, now the main focus is on problems of the experimental study and theoretical analysis of the physical properties. Amorphous alloys of the Fe–Zr system at concentrations close to the eutectic ($Fe_{90}Zr_{10}$) are especially interesting since the magnetic structure and a whole range of properties have an anomalous and, from the point of view of present ideas, even a contradictory nature. Neutron diffraction studies[1,2] show that there is no long-range ferromagnetic order in them, while from magnetic measurements in these alloys, as in usual ferromagnets, a sharp transition temperature to a state with spontaneous magnetization is observed. The temperature dependence of the saturation magnetization is then more gradual than the Brillouin function[3] and its low-temperature part cannot be described by the traditional spin-wave models or by weak Stoner ferromagnetism.[4]

Fe–Zr alloys have spin-glass[5,6] properties which are usually associated with exchange interactions in a system of localized moments. At the same time abrupt Invar anomalies in the thermal expansion[7] and elastic constant[8] appear which, on the contrary, point to a leading role of itinerant magnetism. To this can be added an anomalously large reduction in the magnetic transition temperature under pressure[9] and a giant susceptibility in strong magnetic fields.[10]

Analysis of the results on Fe–Zr alloys is further complicated by the fact that experimental results of different investigations agree poorly with one another. For example, the magnitude of the saturation magnetization which is measured with high accuracy and is insensitive to small variations in chemical composition, varies between the limits of $\approx 20\%$ according to the summary of results given by Unruh and Chien.[11] This complicates the comparison of results obtained by different methods which is very necessary for the development of model representations.

We note that the appreciable scatter in experimental results on the magnetic properties is not only observed for Fe–Zr alloys. The reason for the divergences has been analyzed by Cowlam and Carr.[12] The point is that the specimens studied in different investigations are, in general, not structurally equivalent. Alloys amorphous in structure differ in the degree of structural relaxation. This is determined in the first place by the temperature and rate of solidification of the melt, by details of the preparation technique and by the thermal prehistory of the specimens of the amorphous alloys studied. Investigation of structural relaxation is an independent problem and standardization of specimens according to this parameter is not possible at present. Thus, to obtain comparable results it is, in principle, essential to study one and the same specimens by different experimental methods.

The present work is devoted to a study of the magnetism and the nature of the Invar anomaly in the amorphous alloy $Fe_{90}Zr_{10}$. The temperature dependences of the thermal expansion, saturation magnetization and also of the hysteresis loop and Mössbauer spectrum of ^{57}Fe nuclei were measured on single specimens. All the results indicate that the immediate surroundings determine the magnetism of the Fe atoms. As the temperature is raised part of the Fe atoms undergo a transition to a state with small magnetization which is accompanied by a corresponding decrease in atomic volume, producing the Invar expansion anomaly. The topological distribution of such Fe atoms and Zr atoms leads to the formation in the alloy of "weak magnetic layers," bounding finite magnetic clusters. Near the Curie temperature these clusters possess superparamagnetic properties.

2. EXPERIMENTAL RESULTS AND DISCUSSION

The alloy specimens were produced by the method of spin-casting of the melt in a gaseous helium atmosphere at the outer cylindrical surface of a rapidly rotating roller-cooler. They were sections of ~ 2 mm wide foil of thickness ~ 20 μm. The billets for the spinning were melted in vacuum by an induction method from high-purity materials. The composition of an alloy is given by the results of chemical analysis of the foil. The phase and structural composition of specimens was monitored by x-ray diffraction and by the method of Mössbauer spectroscopy with the recording of conversion electrons. From the latter could be obtained the Mössbauer spectra of the surface layers (~ 5000 Å) of the amorphous specimens, in which structural relaxation and crystallization first develop. The state of the surface layers is especially important for Fe–Zr alloys in connection with the tendency of the material to oxidation, which leads to depletion of the foil in zirconium.

According to the x-ray results the specimens had an amorphous structure and crystalline phases were not detected in the bulk Mössbauer absorption spectra. In the spectra

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of the surface layers on the side of the foil in contact with the cylinder on spinning, bcc Fe lines with a relative intensity of ~20% were found. In other respects the spectrum of the surface and bulk of the alloy agreed completely.

Thermal expansion was studied with a 'Linseitz' dilatometer, fitted with a special cell for measuring the length of thin sections of foil on sandwich specimens of length ~50 mm at temperatures 78–300 K. After the dilatometer measurements the specimens were further used for Mössbauer and magnetic investigations, which were carried out in the temperature range 4.2–320 K. The saturation magnetization in fields up to 4.3 T and hysteresis loops were obtained with a vibration magnetometer, calibrated with pure nickel, on specimens of dimensions $2\times4\times1.5$ mm, made up of sections of foil. The specimen was vibrated at a frequency of ~70 Hz in a heat exchanger placed in a superconducting solenoid immersed in a liquid helium bath. Two measuring coils were placed in the bath coaxially with the oscillation and magnetic field directions. The specimen temperature was set, and stabilized by controlling the flow of liquid helium through the heat exchanger with an additional automatic heating of the heat-exchange gas. A gold-iron thermocouple in contact with the specimen was used as the sensor. The specimen temperature was maintained to an accuracy of $\pm$ 0.3 K.

The investigation of the Mössbauer spectra was carried out on a usual electrodynamic-type spectrometer with a ^{57}Co(Cr) source. The spectrometer was calibrated against pure iron spectra. The width of the outermost lines of the spectra was not more than ~0.30 mm/s. The specimens for Mössbauer studies were also gathered from foil sections used for the dilatometric measurements. The temperature investigations were carried out in an evaporation cryostat with automatic control of the flow of liquid helium or nitrogen, according to the reading of a platinum resistance thermometer. Germanium semiconductor temperature sensors were used below 20 K. When measuring spectra the uncertainty in temperature relative to that set was $\pm$ 0.5 K.

The solid line in Fig. 1 shows the temperature dependence of the relative elongation of a specimen. It can be seen that the $Fe_{90}Zr_{10}$ alloy has a clearly visible Invar anomaly of thermal expansion. The dimensions of the specimen decrease with increasing temperature and the linear expansion coefficient has a negative value. The anomalous contraction

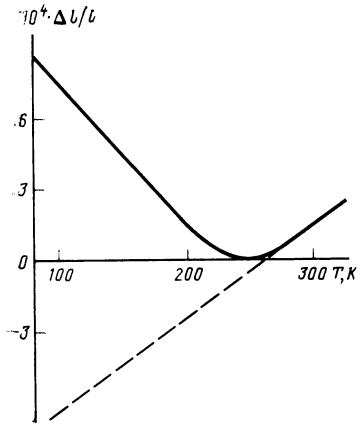

FIG. 1. Temperature dependence of the relative extension.

of the specimen depends linearly on temperature to a good accuracy; above ~250 K it changes to a "normal" expansion. The dashed straight line in Fig. 1 shows the contribution to the elongation from anharmonic thermal vibrations of the atoms of the alloy and is obtained by extrapolating the full curve from temperatures >250 K for which there is no Invar anomaly. A measure of this anomaly is the magnitude of the bulk spontaneous magnetostriction (ω_S) which is determined by the difference between the ordinates of points on the full and dashed lines for a fixed temperature.

Typical hysteresis loops at 4.2, 27.5 and 77.5 K are shown in Fig. 2a, c and d for specimens cooled to 4.2 K in the absence of a magnetic field. A hysteresis loop at 4.2 K is shown in Fig. 2b for a specimen cooled from a temperature ~96 K in an external field of strength 1 T. On raising the temperature, hysteresis practically disappears (see Fig. 2a, b and c), while cooling in an external field leads to a shift of the loop opposite to the direction of the applied external field. As well as the shift, a small reduction in the coercive force is observed and a contraction of the hysteresis loop. These results show that in an amorphous alloy with a random distribution of local magnetic anisotropy a macroscopic unidirectional magnetic anisotropy appears under the influence of an external magnetic field. Similar results were obtained earlier

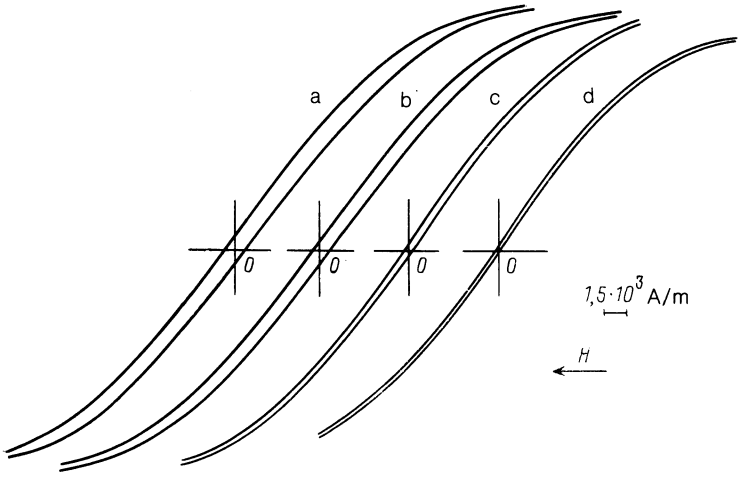

FIG. 2. Hysteresis loops for the alloy $Fe_{90}Zr_{10}$ at temperatures a) 4.2 K; c) 28.5 K; d) 77.5 K; b) at 4.2 K after cooling in a magnetic field.

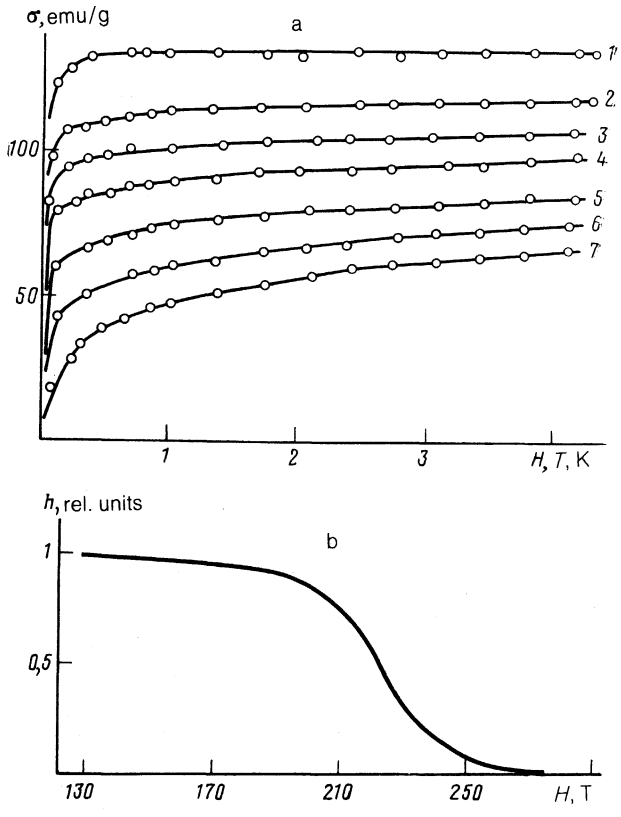

FIG. 3. a—magnetization curves for the alloy $Fe_{90}Zr_{10}$ at various temperatures: 1) 4.2 K; 2) 98.6 K; 3) 131.5 K; 4) 155.3 K; 5) 190.3 K; 6) 213 K; 7) 239 K; b—temperature dependence of the magnetization measured in small fields.

by Hiroyoshi and Fukamichi[6] on the alloy $Fe_{92}Zr_8$.

The experimental dependences of the magnetization σ on the external field H for different temperatures are shown in Fig. 3. It can be seen that magnetic saturation is not reached even at 4.2 K in the largest external fields. On increasing the temperature the magnetization measured in high fields falls slowly and preserves an appreciable magnitude at temperatures for which h, measured in a small field, is close to zero (Fig. 3b). Figure 3b shows the transition to the state with spontaneous magnetization, measured in the absence of an external magnetic field. In appearance, this transition corresponds to a usual ferromagnet with Curie temperature $T_c = 220.5$ K. The procedure for a quantitative determination of the spontaneous magnetization σ from its field dependence is fairly complicated.

In the present work the value of the spontaneous magnetization below the Curie temperature was determined, as in the case of a usual ferromagnet, by linear extrapolation of the high-field parts of the magnetization curves of Fig. 3a to zero field. At higher temperatures the magnetization was calculated from the curves of Fig. 3 by the least squares method, according to the formula:

$$M(H)=M_0\left[\operatorname{cth}\frac{\mu H}{kT}-\left(\frac{\mu H}{kT}\right)^{-1}\right]+\chi_0 H. \qquad (1)$$

The first term represents the magnetization of a system of superparamagnetic particles or clusters with magnetic moment μ at temperature T in a magnetic field H, M_0 is the magnetization of a system in the stabilized state, k is Boltzmann's constant.

TABLE I.

T, K	$\mu\cdot10^3$, μ_B	$\chi_0\cdot10^{-3}$, emu/g·Oe
220	34,5	1,15
274	28,2	1,02
332,8	3,5	0,9

The superparamagnetic behavior of the amorphous alloy $Fe_{90}Zr_{10}$ was found by Fries *et al.*[13] and by Yamamoto *et al.*[14] who studied the influence of external fields on the Mössbauer spectra. The second term in Eq. (1) takes account of the paraprocess in a system of stabilized superparamagnetic clusters and also the contributions to the magnetization induced by the magnetic field. In the analysis, the field region corresponding to saturation was left out of consideration. The phenomenological formula (1) was used earlier[15] to describe the magnetization of cluster spin glasses in Cr–Fe alloys. The magnitudes of μ and χ_0 are given in Table I, the relative values of M_0 are shown by the open circles in Fig. 4. In addition, values of the relative spontaneous magnetization are given in Fig. 4, obtained by linear extrapolation to zero field of the curves of Fig. 3a, corresponding to temperatures below the Curie temperature.

The solid line in Fig. 4 is the relative magnetization σ/σ_0 calculated by the molecular-field method with fluctuations of exchange interactions in an amorphous alloy:

$$\sigma/\sigma_0={}^1/_2\{B_S[(1+\Delta)x]+B_S[(1-\Delta)x]\},\ T<T_c\,. \qquad (2)$$

Here

$$x=(3S/(S+1))\,(T_c/T)\,(\sigma/\sigma_0);\quad \Delta=[\overline{\delta J^2}/\bar{J}^2]^{1/2}$$

is the relative mean square width of the distribution of exchange integrals, δJ is the fluctuation in exchange integral, $\bar{J}$ is the mean value; the quantity $\sigma_0 = 1.24\,\mu_B$ is the saturation magnetization per atom at 4.2 K, expressed in Bohr magnetons; $S = 1$ is the atomic spin, B_S is the Brillouin function corresponding to the spin S. The quantity $\Delta\approx0.6$ coincides with that obtained by Ohnuma *et al.*[3] for the same composition. We note that the value of Δ is anomalously

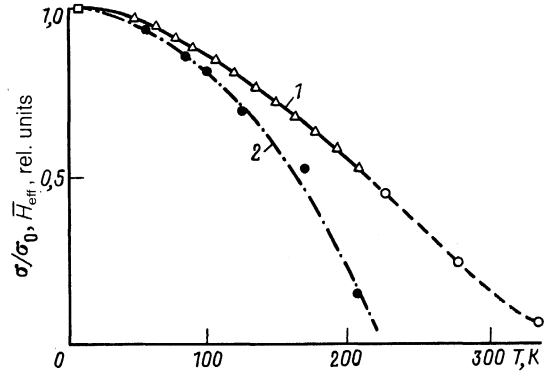

FIG. 4. Temperature dependence of (△) the relative magnetization, (●) the relative mean effective field and (○) the magnitude of M. The full line is calculated according to Eq. (2), the dashed and dashed-dot lines are the experimental curves.

large compared with the analogous values for other amorphous alloys.[17]

The solid and dashed curves in Fig. 4 join up with one another satisfactorily, justifying the use of the model phenomenological expression (2) to describe the magnetization at temperatures above the Curie point. From the means for obtaining both curves it is clear that they represent the stabilized magnetization of an amorphous alloy over the whole temperature region where the Invar expansion anomaly is observed.

To obtain instantaneous values of the magnetization of an Fe–Zr alloy, Yamauchi *et al.*[18] used the Arrott-Belov relation ($M^2 \propto H/M$). However, this form of representing the results in the case considered seems highly problematical. In fact Beck and Kronmüller[19] noted the necessity of including additional terms in this dependence, owing to the strong magnetic inhomogeneity of the alloy. In the present work the mean effective field ($\overline{H}_{\text{eff}}$) is used to estimate the instantaneous value of the magnetization in the Mössbauer spectra. The value of $\overline{H}_{\text{eff}}$ was determined from the distribution of effective fields $P(H_{\text{eff}})$ according to the formula

$$\overline{H}_{\text{eff}} = \int P(H_{\text{eff}i}) H_{\text{eff}} \, H_{\text{eff}} \ . \qquad (3)$$

The functions $P(H_{\text{eff}})$ are the probability density for the distribution of H_{eff} in the spectra. They were obtained from the experimental spectra by the standard method. The left-hand halves of the Mössbauer spectra for different temperatures and the corresponding functions $P(H_{\text{eff}})$ are shown in Fig. 5. The solid curves in Fig. 5a show the half-spectra calculated according to the function $P(H_{\text{eff}})$. The calculated spectra agree well with the experiments. In the analysis of the experimental spectra the asymmetry of the right and left halves of the spectra was neglected, and the small apparent quadrupole splitting was not taken into account. The widths of the Lorentzian lines of the separate components were 0.30 mm/s and the amplitudes were in the ratio 3:2:1.6. This ratio was found from the areas of the corresponding lines of the spectrum at 4.2 K. The small changes in the relation shown above have practically no influence on the form of $P(H_{\text{eff}})$.

The functions $P(H_{\text{eff}})$ were obtained earlier[21–23] for amorphous Fe–Zr alloys of close composition. Although the details of $P(H_{\text{eff}})$ in all these works do not coincide completely, owing to differences in the state of the specimens and in the methods of decomposing the Mössbauer spectra, the behaviors of $\overline{H}_{\text{eff}}(T)$ are practically identical. The relative values of $\overline{H}_{\text{eff}}(T)$ are shown in Fig. 4 (full circles). In order to take account of the small ($\sim 2\%$) discontinuous increase in $\overline{H}_{\text{eff}}$ on going to helium temperatures, found by Ghafari *et al.*[21] the value $\overline{H}_{\text{eff}}$ (4.2 K) = 257 kOe was taken as 1.02. It can be seen that the value of $\overline{H}_{\text{eff}}(T)$ and, consequently, the instantaneous magnetization at low temperatures (up to ~ 40 K) are close to the corresponding values of the stabilized magnetization, while with increasing temperature the graphs of these dependences diverge. The instantaneous magnetization goes to zero at the critical point, while the stabilized magnetization has a noticeable value at $T = T_c$.

We will now analyze the form of the graphs of the $P(H_{\text{eff}})$ dependence, which was not considered before. The results[21–23] refer mainly to low temperatures, where $P(H_{\text{eff}})$ is simply a symmetrical peak centered at $\overline{H}_{\text{eff}}$ (see Fig. 5b). Up to temperatures of 50–60 K the width and intensity of

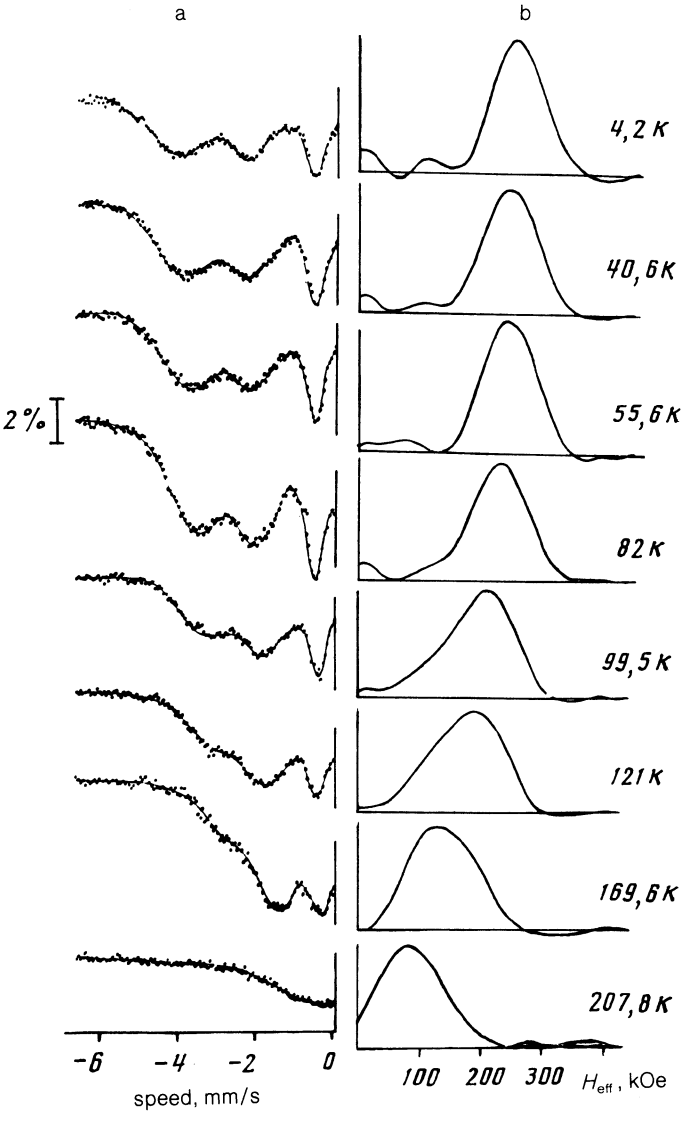

FIG. 5. a—Mössbauer spectra of the alloy $Fe_{90}Zr_{10}$; the points are experimental, the full curves are calculated according to $P(H_{\text{eff}})$; b—curves of the distribution of effective fields.

this maximum does not change within the limits of accuracy. At higher temperatures the plot of the function $P(H_{\text{eff}})$ becomes asymmetrical. The main peak acquires on the side of small H_{eff} a shoulder whose intensity increases with rise in temperature. We note that the form of the function $P(H_{\text{eff}})$ in the spectra of Fe–Ni Invar alloys changes in a similar manner on raising the temperature.[24]

The magnetic state of the Fe atoms corresponding to the shoulder of the $P(H_{\text{eff}})$ curve differs strongly from the most probable, to which corresponds the main maximum in $P(H_{\text{eff}})$. These atoms are characterized by a relatively small magnetization which is due to the small magnitude of the atomic magnetic moment or of the exchange molecular field. It is well known that the Mössbauer spectra of ^{57}Fe nuclei are sensitive to the composition and radius of the first coordination sphere of Fe atoms. Thus Fe atoms with small magnetization correspond to a certain type of immediate surroundings. The determination of the relative proportion of such atoms from the intensity of the $P(H_{\text{eff}})$ shoulder is rather complicated as a result of poor resolution of the separate

$P(H_{\text{eff}})$ peaks. The point is that the interatomic-spacings fluctuations which are characteristic of amorphous alloys, and also the influence of distant coordination spheres, blur the magnetic states of Fe atoms with different types of immediate surroundings and lead to their mutual overlap. This is reflected in the strongly smoothed-out appearance of the $P(H_{\text{eff}})$ function. At the same time the intensity of the shoulder can be found correctly for a number of $P(H_{\text{eff}})$ curves in Fig. 5b by separating off the main maximum, the width and shape of which are known from the form of $P(H_{\text{eff}})$ at low temperatures. It is probable, as in Fe–Ni Invar alloys,[24] that the corresponding Fe atoms are responsible for the Invar expansion anomaly in $Fe_{90}Zr_{10}$. This question is considered in more detail below.

At present a common opinion on the features of the magnetism of alloys of the Fe–Zr system has not been put together. Neutron diffration investigations[1,2,25] show that there is no long-range ferromagnetic order in these alloys, the magnetic correlation length stays finite at the passage through the Curie temperature and does not exceed ~ 200 Å on further cooling to helium temperatures. Magnetic measurements and Mössbauer spectroscopy results[22] also indicate the inhomogeneous, cluster nature of the arising ferromagnetism.

At low temperatures the alloys probably go over into a spin glass state,[21] which is characterized by a complete freezing-in of the magnetic moments. The longitudinal components of the moments directed along the local easy axis of magnetization are collinear, while the perpendicular components have a random distribution. It is assumed that the formation of a spin glass is produced by mixed ferromagnetic and antiferromagnetic interactions between Fe atoms. The freezing-in temperature for the alloy $Fe_{90}Zr_{10}$, according the Ghafari *et al.*[21] is 35–40 K. At higher temperatures the longitudinal components remain collinear, as in a usual ferromagnet, with the same characteristic that the local axis of magnetization preserves its direction within the limits of the correlation length, while at large distances its direction is randomly distributed.

We note that the connection between the Invar anomaly and the elements of the magnetic structure have so far not been discussed. It is, in general, considered that the anomalous expansion of amorphous alloys is quantitatively described by the theory of weak itinerant ferromagnetism,[26] which predicts quadratic dependences of magnetization on temperature and of spontaneous magnetostriction on the magnetization. In fact, for a number of amorphous alloys[27] the theory describes satisfactorily the behavior of $\omega_S(T)$ in a limited temperature interval. However, it can be seen from Fig. 1 that for the alloy studied the function $\omega_S(T)$ is linear to a good approximation. The large magnetovolume effect at temperatures above the Curie point also does not agree with this theory. We stress that a temperature variation of atomic moment is a necessary condition for the appearance of the Invar expansion anomaly in metallic ferromagnets.[28]

The unidirectional anisotropy, which arises in the alloy studied on cooling in a magnetic field to helium temperatures, is a characteristic feature of spin glasses. The coincidence of stabilized and instantaneous magnetization, and the symmetrical appearance of plots of $P(H_{\text{eff}})$ in turn indicate the complete freezing-in of atomic moments. The transition temperature estimated from the disappearance of unidirectional anisotropy, the behavior of $P(H_{\text{eff}})$ and of the magnetization is 35–45 K, which agrees completely with the literature data cited above. These results correspond to a picture of localized moments with competing exchange interactions. We note that the spin glass regime arises in an itinerant ferromagnet if one takes into account the influence of the local environment on the size of the moments and the nature of their interaction.[29] Kakehashi[29] proposed that a spin glass would be formed in amorphous Fe–Zr alloys by such a mechanism.

In the interval between the freezing temperature and the critical point in the alloy studied the Fe atoms appear with relatively small magnetization, and differences arise between the stabilized and instantaneous magnetization and increase with a rise in temperature. The number of Fe atoms which correspond to the $P(H_{\text{eff}})$ shoulder also increases. The change in magnetic structure is accompanied by appreciable reduction in bulk magnetostriction. These results can be explained by features of the spin dynamics and magnetism of Fe atoms. It is interesting that in the alloy $Fe_{92}Zr_8$ (Ref. 25) under these conditions a reduction in correlation length, corresponding to the spin dynamics, was observed by neutron diffraction.

Clearly the magnetic structure of the alloys discussed can be represented in the following way. Since direct exchange is the main one in concentrated magnetic systems, some neighboring Fe atoms from the number which undergo competing exchange form topological layers which are formed by the boundaries of interacting magnetic clusters of finite dimensions. The total moments of the clusters relax slowly, their instantaneous magnetization is reflected in the distribution $P(H_{\text{eff}})$, since the measuring time in the Mössbauer spectroscopy method is only 10^{-7}–10^{-8} s. In an external magnetic field the total moments are stabilized and the difference noted between the instantaneous and stabilized magnetization arises. On raising the temperature the fraction of Fe atoms in the layers increases and the size of the clusters correspondingly decreases. It is natural that upon formation of the layers a reduction in atomic moment should be expected for the corresponding Fe atoms, which would lead, in turn, to a reduction in atomic volume and a corresponding contribution to the spontaneous magnetostriction.

We will illustrate these arguments by a quantitative estimate, under the assumption that the fraction of Fe atoms in finite clusters is given by the intensity of the main $P(H_{\text{eff}})$ maximum, while the Fe atoms producing the Invar anomaly correspond to the shoulder of the $P(H_{\text{eff}})$ peaks. We will find the mean magnetic moments ($\bar{\mu}_{\text{Fe}}$) for Fe atoms corresponding to the $P(H_{\text{eff}})$ shoulder according to the values of the mean effective fields, since for amorphous Fe–Zr alloys they are proportional to one another.[22] We shall determine the coefficient of proportionality from the ratio $\bar{H}_{\text{eff}}/[\mu_0(\mu_0+1)]^{1/2}$ at 4.2 K with the values $H_{\text{eff}} = 257$ kOe and $\mu_0 = 1.37\,\mu_B$. The latter quantity is the saturation magnetization per Fe atom.

In this way the function $P(H_{\text{eff}})$ gives directly the distribution of local moments of Fe atoms with a coefficient of proportionality $\simeq 143$ kOe/μ_B. For temperatures of 82 and 99.5 K, for which the decomposition of $P(H_{\text{eff}})$ is accomplished fairly correctly, the values of $\bar{\mu}_{\text{Fe}}$ are 1.0 and 0.75 μ_B,

the fractions of the corresponding Fe atoms are $n = 0.14$ and 0.21, the decrease in magnetostriction $\Delta\omega_S = 5.6\times 10^{-4}$. The atomic moment and magnetostriction are related by a quadratic dependence which follows from spin fluctuation theory (see, for example, Silin and Solontsov[30]) and has been confirmed experimentally more than once on crystalline systems.[31,32] Then

$$\Phi\Delta\omega_S = C\frac{\Delta V}{V} n\mu_{Fe}^2|_{99,5\ K} - C\frac{\Delta V}{V} n\mu_{Fe}^2|_{82\ K}, \qquad (4)$$

where $C = 0.9$ is the Fe concentration, $\Delta V/V$ is the relative change in atomic volume, Φ is the structure factor which is determined by the coordination number and symmetry of the immediate surroundings. We take the value $\Phi \approx 0.74$, the same as for a fcc lattice, since the coordination number for Fe atoms in the amorphous alloy $Fe_{90}Zr_{10}$ is equal to 11.6 (Ref. 33). We obtain from these data $\Delta V/V = 1.9\times 10^{-2}/\mu_B^2$, which is in good agreement with the existing theoretical and experimental estimates of $(1\text{–}3)\times 10^{-2}/\mu_B^2$ (Ref. 34).

Above the Curie temperature the interaction decreases so much that the clusters become superparamagnetic. With an increase in temperature the clusters are reduced in size (see Table I) and the magnitude of ω_s decreases smoothly. It is probable that an excitation of all the new Fe atoms into a state of small moment takes place, which on the one hand makes a contribution to the bulk magnetostriction equal to $\approx 1.9\times 10^{-2}/\mu_B^2$ per Fe atom, while on the other breaks the passage for direct exchange, thereby reducing the cluster size. Such Fe atoms are evidently easily polarized by an external magnetic field, which is indicated by the giant value of χ_0, which exceeds the high-field susceptibility at 4.2 K by an order of magnitude.[10] However, stabilization of the total moments of finely dispersed superparamagnetic clusters in an external field can also explain the large value of χ_0.

The anomalous magnitude of Δ (see Fernandez-Baca *et al.*[2]), obtained on calculating the stabilized magnetization, when the influence of the cluster magnetic structure can be neglected, provides an additional indication of the antiferromagnetic interactions in the alloy studied. This quantity is twice the value of Δ for the amorphous Invar alloy $Fe_{83}B_{17}$ (Ref. 17). Since the latter is a less concentrated alloy one would expect for it a large dispersion in the value of the exchange interactions. However, the effective width of the distribution can grow appreciably if there are two well separated groups of interactions in the alloy (positive and negative). In other words, the anomalous value of Δ possibly indicates a two-level excitation of Fe atoms in Fe–Zr alloys. It is probable that this is the cause of the analogy between the properties of amorphous Invar Fe–Zr alloys and crystalline Invar Fe–Ni alloys, which in many respects are considered as two-level systems.[35]

Calculations "from first principles"[36] also show that the electron densities of states of non-magnetic amorphous iron and fcc Fe are similar. Band calculations[37] for fcc Fe give as a result a reduction of atomic moment and a change from ferromagnetic to antiferromagnetic order over a narrow interval of interatomic spacings. Fluctuations of interatomic distance, which are characteristic for the amorphous state, can thus produce competition between ferromagnetic and antiferromagnetic interactions in concentrated amorphous alloys, as was first suggested by Masumoto *et al.*[38] Dilatations around Zr atoms could be another factor leading to the relative strengthening of ferromagnetic over antiferromagnetic interactions for the alloy studied, since Zr atoms have a considerably greater atomic radius than Fe atoms.

3. CONCLUSIONS

In the present work the magnetic properties, thermal expansion, and Mössbauer spectra of the amorphous Invar alloy $Fe_{90}Zr_{10}$ have been studied on one and the same specimens. This enabled the main elements of the magnetic structure determining the anomaly in the bulk magnetostriction to be revealed and quantitative relationships to be established. The Invar anomaly in the alloy studied is produced by competing positive and negative exchange interactions between Fe atoms, which arise as a result of fluctuations in the interatomic spacings. The existence of two forms of interactions in a concentrated alloy requires further investigations. Amorphous alloys are the most suitable materials for an experimental verification of theoretical calculations of the magnitude of the magnetic moment and its dependence on atomic volume. The main difficulty here apparently resides in the study of atomic correlation in amorphous alloys, which can be modified to a considerable extent by the composition and the dimensions of the local atomic configuration.

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