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Hyperfine interactions and local environment effects in Fe_xNi_{100-x} ($x = 55$–67) Invar alloys: ^{57}Fe Mössbauer spectroscopy data at 5 K

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ABSTRACT

A systematic study of the magnetic hyperfine field distribution for ^{57}Fe in the Invar alloys Fe_xNi_{100-x} ($x = 55$, 60, 63, 65 and 67) have been performed by Mössbauer spectroscopy technique at 5 K. The composition dependences of the magnetic hyperfine fields (B_{hf}), isomer shifts and relative intensities of the magnetic subspectra were measured and analyzed. The reliable data on the correspondence between the B_{hf} magnitude and the type of locale atomic configuration were obtained. It is confirmed that the Fe–Ni Invar alloys in their ground state are predominantly collinear ferromagnets with well-defined atomic magnetic moments. Particular emphasis has been placed on the low-field (LF) component of the distribution ($B_{hf} = 1.4$ and 2.5 T) which is considered as corresponding to the Fe sites with the antiferromagnetic (AFM) alignment of the magnetic moment. The most striking feature of the LF component is the anomalous positive isomer shift that corresponds to a large reduction of the local electron density at the Fe sites. It may be proposed that the volume effect is one of the plausible reasons for the increase in the IS value for LF components. In this case, we should suggest that the formation of the AFM sites leads to some increase in the local atomic volume. The possible influence of the competition between energetically satisfied and unsatisfied exchange bonds on the stability of the AFM states of the Fe atoms is briefly discussed.

1. Introduction

One of the most remarkable phenomena observed in magnetic alloys is the Invar effect which consists of the vanishing of the thermal expansion coefficient of the fcc Fe–Ni alloys at Ni concentrations around 35 at.% and over a wide temperature range below the magnetic ordering temperatures. The macroscopic properties of the Invar alloys have been investigated in detail, however the microscopic mechanism of the Invar effect still has not got a commonly accepted explanation. There is no doubt that the Invar effect is strongly related to the magnetic ordering of the alloys but there is no general consensus on the origin of the effect. Although the origin of the Invar effect has been extensively theoretically investigated, it is still controversial. Among the theoretical models of the Invar effect, the theories based on the correlation between the volume and the magnitude of the Fe magnetic moment hold much favor [1–4]. It is believed that the Invar effect is related to a loss of local moment magnitude and an associated contraction occurring as the temperature is increased. In the theory, the electron configurations of the Fe atoms should change through the transition from the high-moment state to the low-moment one. However, at the same time it has been shown [5,6] that the basic macroscopic properties of the Invar alloys can be explained by theories in which Invar is predominantly a ferromagnetic alloy, having local magnetic moment magnitudes that are not affected by temperature. An alternative approach to the Invar problem is based on an assumption of non-collinear magnetic structure of the Invar alloys [7,8]. In terms of this theory, the magnetic structure of the alloy is characterized by the existence of nearly degenerate non-collinear states with differing magnetic moments and volumes. In the “frustration” model of the Invar alloys [9–11], particular attention has been paid to the antiferromagnetic exchange interaction Fe–Fe. If the Invar alloy is a predominantly collinear ferromagnet, the antiferromagnetic Fe–Fe exchange bonds are not energetically satisfied. As a result, a magneto-volume effect appears which is accompanied by an anomalous expansion of the lattice at low temperatures. The several theories of the Invar effect were recently critically reviewed [11]. None of the above-mentioned models have been unambiguously confirmed by experiment. In particular, the polarized neutron results obtained in the temperature range from 100 to 600 K [12] seem to be incompatible with the two-state models. The direct measurements by the neutron scattering technique showed [13,14] that the Invar Fe–Ni alloys are collinear ferromagnets over a wide range of temperatures.

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A common feature to all the aforementioned theories is that the possible local effects have been largely ignored. In other words, it is assumed that the magneto-volume striction (expansion or contraction) is uniform down to the microscopic scale. However, the Fe–Ni Invar is a concentrated random alloy in which the local environment effects may play a crucial role because the magnetic states of the Fe atoms as well as the structural parameters can be strongly influenced by the type of the local atomic configuration. For example, from the theoretical estimates [9] one would expect that the Fe sites surrounded by 10 or more Fe nearest neighbors have an antiferromagnetic alignment of its magnetic moment. Unfortunately, little is known about the local effects in the Fe–Ni Invar alloys. However, the recent experiments provide unambiguous evidence for the existence of such effects. Experimentally, it was found that the mean separation of Fe–Fe neighbor pairs is expanded relative to the average lattice [15]. The direct evidence for the existence of the locale environment effects has been obtained from the elastic diffuse scattering of neutrons [16]. For the $Fe_{65}Ni_{35}$ alloy, the results suggest the existence of microclusters with the average size of 2–5 nm. The features of the clusters are found strongly correlated with the behavior of the Invar alloys as a function of temperature and composition. It is important to emphasis that the formation of the clusters is directly related to the local deformations of the lattice. Recently, a theoretical study of static atomic displacements in the $Fe_{65}Ni_{35}$ alloy has been performed [17]. It was found that the Invar alloys are characterized by a huge dispersion of both the interatomic distances and the nearest neighbor exchange parameters. The individual static displacements can be quite large; for the Fe–Fe bonds, the difference in the interatomic distances can reach a value of up to 9%. Obviously, so large local displacements should have a strong influence on the behavior of the Invar alloy as a whole.

A detailed knowledge of the properties of electron states of the Fe atoms on microscopic level is necessary for a further understanding of the nature of the Invar effect. So far, there are few data dealing with this problem. As a result, the physical grounds, which are needed to make a decision between alternative models of the Invar effect, are still lacking. Unfortunately, experimental tools to observe directly magnetic behavior of particular atoms in disordered alloys are very limited. At present seemingly that the Mössbauer spectroscopy is a uniquely suited technique for this purpose, since its site selectivity allows probing the electron and magnetic properties of the Fe atoms reside in the non-equivalent sites in the crystal. The technique offers a possibility to observe spin configurations of different types and to classify these states by using an analysis of the hyperfine parameters. In addition, for the Invar problem, an important parameter is the isomer shift which value is a source of information on both the electron configuration of the Fe atoms and the variations of the atomic volume [18,19].

The Mössbauer spectroscopy technique has been used in the Invar alloys studies repeatedly. The basic results were deduced from the analysis of the hyperfine field distributions (HFD) [20–22]. It was found that, at low temperatures, more then 90% of the full intensity forms the main maximum (MM) of HFD [22,23]. The components of MM correspond to the Fe atoms located in the ferromagnetic atomic configurations. For these configurations, the values of the hyperfine field (B_{hf}) at the central Fe site exceed 20–25 T. The width of MM is determined by statistical variations of the number of the Fe atoms in the nearest environment of the central Fe atom [20,23,24]. Apart from MM, the rather small low-field (LF) component is present for which the B_{hf} magnitude not exceeds 5–10 T. The presence of the LF component in the Mössbauer spectra of the Fe–Ni Invar alloys is recorded repeatedly (for examples, see Refs. [22,23,25]) but this component has never been studied in detail. Until now, most research has focused on the behavior of the Fe atoms in certain ferromagnetic configurations belonging to MM. Little attention is given, however, to other components of the spectra that may play an important role. Taking into consideration the above-mentioned possibility of the local effects, a close examination of all spectral components appears especially important. The careful study of the behavior of the parameters of the spectra as a function of composition is also very important.

In this paper we present the results of a systematic study of the magnetic ground state (at $T = 5$ K) of the Fe–Ni Invar alloys in the concentration range of 55–67 at.% Fe by means of the ^{57}Fe Mössbauer spectroscopy. The particular aim of this work is detailed measurements of the concentration dependences of the main parameters of the Mössbauer spectra (the magnetic hyperfine fields, the relative intensities of magnetic subspectra and the isomer shifts). As a result, the reliable data on the correspondence between the B_{hf} magnitude and the type of the atomic configuration were obtained. A special attention has been paid to the LF components of the hyperfine field distribution, which may be assumed to relate to local environment effects.

2. Experimental

Samples of Fe_xNi_{100-x} (with $x = 55$, 60, 63, 65 and 67) were prepared using the standard procedure which assures production of the disordered Invar alloys with the fcc crystal structure. Alloys ingots were prepared by arc melting in argon using metals with purity not worse than 99.98%. The samples were re-melted several times for homogenization. The ingots were annealed in a quartz tube under a protective argon atmosphere at 1200 K and quenched. Then the ingots were filed into fine powders for Mössbauer measurements. The powder samples were annealed at 1200 K and quenched. In order to check the purity of the alloys the samples were examined by X-ray powder diffraction. Analysis of the data has conformed unambiguously that the samples have expectation fcc structure without visible contamination by the other phase. The lattice parameters were in a good agreement with results given in the literature ([10,26] and references therein). The Mössbauer absorption spectra were measured at 5 K using a ^{57}Co source in a Rh matrix. In order to enhance the effect of resonance absorption and resolution in detecting the Mössbauer radiation, a resonance detector was used. Isomer shifts (IS) are given relative to α-Fe at room temperature.

Two different fitting procedures were applied to the Mössbauer spectra analysis. First, the hyperfine field distributions were calculated by the histogram method. The widths of the histogram intervals were chosen so that would be nearly equal to the instrumental line width. This allowed us to use the direct method for minimizing the χ^2 functional and to eliminate ambiguities associated with smoothing procedure. Second, the spectra were least-squares fitted by a superposition of discrete magnetic subspectra. The line intensity ratios in each sextet were constrained to 3:2:1:1:2:3. All the other parameters (including the relative intensities of the magnetic subspectra and the isomer shifts) were set free in the fitting procedure. The quadrupole shifts of the components of the magnetic subspectra are very small (not more than 0.03 mm/s). Such quadrupole interaction causes only very small asymmetry of the spectra but does not affect the parameters of the spectra appreciably. The number of subspectra required for correct approximation was not fixed but was determined during processing. The velocity resolution was typically 0.11 mm/s/channel. The investigation of the central part of the spectra, where the LF components of HFD are localized, has been performed under specialized conditions with the velocity scale factor of 0.018 mm/s/channel. Below, the alloys are abbreviated by an indication of the Fe concentration only (Fe55, Fe60, etc.).

3. Results

A typical example of the Mössbauer spectrum and corresponding HFD is given in Fig. 1. As a whole, our results for the HFD are rather similar to the previously reported data (see references cited in Section 1). We find that more then 90% of the full intensity form the MM of HFD. For atomic configurations consisting MM, the values of B_{hf} at the central Fe atom exceed 25 T. In addition, for all alloys under consideration, the LF component ($B_{hf} < 5$ T) with the intensity less than 10% is present. It is important to note that, all over from the LF component up to the MM, the hyperfine fields are absent completely. Thus, in the ground state of the Fe–Ni Invar alloys, only two types of the magnetic states of the Fe atoms are present: ferromagnetic states which form the MM's configurations and nonferromagnetic ones (LF components of HFD). As the intensity of the LF component is rather small, this picture is consistent with the assumption that the Invar is predominantly a ferromagnetic alloy

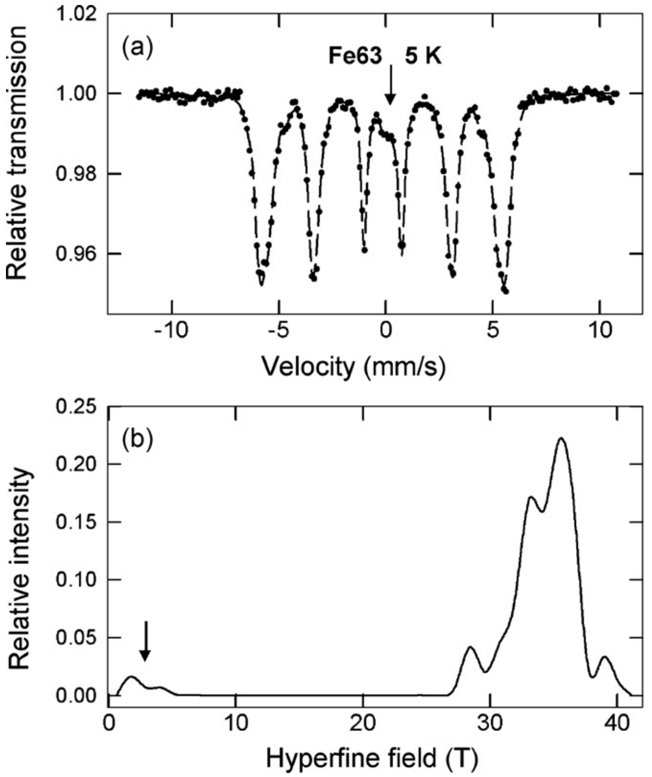

Fig. 1. (a) Mössbauer spectrum of the $Fe_{63}Ni_{37}$ alloy at 5 K and (b) the corresponding function of distribution of hyperfine field. The arrows indicate the position of the LF component.

Table 1

Magnetic hyperfine fields (B_{hf}) and relative intensities (INT) obtained as a result of the approximation of the main maximum of HFD by a superposition of discrete magnetic subspectra at 5 K. The mean-square errors for B_{hf} and INT are equal to 0.02 T and 0.02, respectively. N is the number of the Fe atoms in the nearest environment. For all of the subspectra, the isomer shift is 0.153(5) mm/s (relative to α-Fe at room temperature).

	N						
	10	9	8	7	6	5	4
Fe55							
B_{hf} (T)	38.3	36.6	35.4	34.1	32.7	31.4	29.9
INT	0.02	0.08	0.18	0.22	0.22	0.15	0.10
Fe60							
B_{hf} (T)	38.4	36.5	35.3	34.1	33.0	31.7	30.3
INT	0.04	0.14	0.20	0.24	0.18	0.11	0.05
Fe63							
B_{hf} (T)	38.8	36.9	35.6	34.2	32.9	31.5	30.3
INT	0.05	0.14	0.23	0.22	0.16	0.08	0.04
Fe65							
B_{hf} (T)	38.5	37.1	35.5	34.2	32.9	31.2	29.2
INT	0.04	0.14	0.21	0.21	0.17	0.09	0.06

in which nearly all Fe atoms are present in a single high-moment state [20,23].

3.1. Main maximum of HFD

The shape profile of the MM is determined by statistical variations of the number of the Fe atoms in the nearest environment of the central Fe atom [20,23,24]. Ours measurements of the composition dependence of the MM's profile give an opportunity to obtain the reliable data on the correspondence between the B_{hf} magnitude and the type of locale atomic configuration. The shape of the MM can be well approximated by the superposition of discrete magnetic subspectra. It is known [23,27] that, in disordered Fe–Ni alloys, the value of the magnetic hyperfine field, B_{hf}, can be represented, as a well approximation, by the sum of two contributions as

$$B_{hf} = a\mu_{Fe} + bM(N), \tag{1}$$

where μ_{Fe} is the magnetic moment of Fe atom, M is the net magnetic moment in the nearest environment of the central Fe atom, a and b are constant parameters, N is the number of Fe atoms in the nearest environment. If the Fe moment remains unchanged, the variations of B_{hf} across the MM are determined completely by the change in the number of the Fe nearest neighbors. In this case, a set of the equidistant values of B_{hf} should be observed. The difference in B_{hf} for adjacent subspectra, ΔB_{hf}, corresponds to the replacement of one Fe atom by Ni. The relative intensities of the subspectra should correspond to the binomial distribution W(N). Experimentally, just these regularities have been observed. The results of the approximation of the spectra by the superposition of the distinct magnetic subspectra are present in Table 1 and Fig. 2. The identification of the subspectra (that is the determination of a relationship between the B_{hf} value and the N number) can be deduced from the analysis of the concentration dependence of the relative intensities of the magnetic subspectra. The identification is rather simple because the different components of the binomial distribution W(N) have essentially different dependences on the Fe concentration. For example, in going from Fe55 to Fe63, the probability W(6) decreases from 0.21 to 0.15, while W(9) increases from 0.09 to 0.17. In Fig. 2a the concentration dependence for three subspectra is shown in comparison to W(N), N = 6, 8 and 9. It is seen that the identification of the subspectra is quite unambiguous. It should be noted that our identification of the subspectra is different essentially from that proposed in Ref. [20]. This disagreement may be easily explained. In Ref. [20] the fitting procedure was performed for the Fe67 alloys only. However, as it seen from Fig. 2, at such a high Fe concentration, the really observed relative intensities of subspectra deviate largely from the binomial distribution.

Two crucial results must be emphasized. Firstly, as seen from Table 1, for Fe55, Fe60, Fe63 and Fe65 alloys, the shape of the MM is approximated by the superposition of the magnetic subspectra with the same set of the B_{hf} values. For a given atomic configuration, the B_{hf} value appears to be essentially independent of the Fe concentration. Secondly, the B_{hf} values for adjacent atomic configurations are nearly equidistant. On the average, the difference in B_{hf} for adjacent subspectra, ΔB_{hf}, is equal to 1.4(3) T. These two regularities strongly suggest that the atomic magnetic moments appear to be essentially independent of both the composition and the type of the local atomic configuration. Also, we may conclude that the configurations comprising MM have an essentially collinear magnetic structure. We cannot entirely rule out the presence of some deviations from collinearity. However, any non-collinearity, if existed, should be small. Assuming that the magnetic moment of Fe and Ni atom is equal to 2.8 and 0.6 μ_B, respectively, the coefficients a and b in Eq. (1) are found to be 7.2(3) and 0.63(3) T/μ_B, respectively. These values are rather close to those previously reported in Refs. [23,27].

As seen from Fig. 2, for the alloys with the smaller Fe concentrations, the close agreement between the measured and calculated relative intensities of the subspectra is observed. As the Fe concentration is increased, some discrepancies appear, the origin of which will be discussed below in Section 4. Here we focus on the fact that the subspectrum N = 11 has never been observed. For all of the subspectra comprising MM, the IS value is essentially identical. At 5 K, the observed IS value is 0.153(5) mm/s. After the second order Doppler shift correction (according to the procedure described in [10]) the IS value becomes 0.26 mm/s which is very

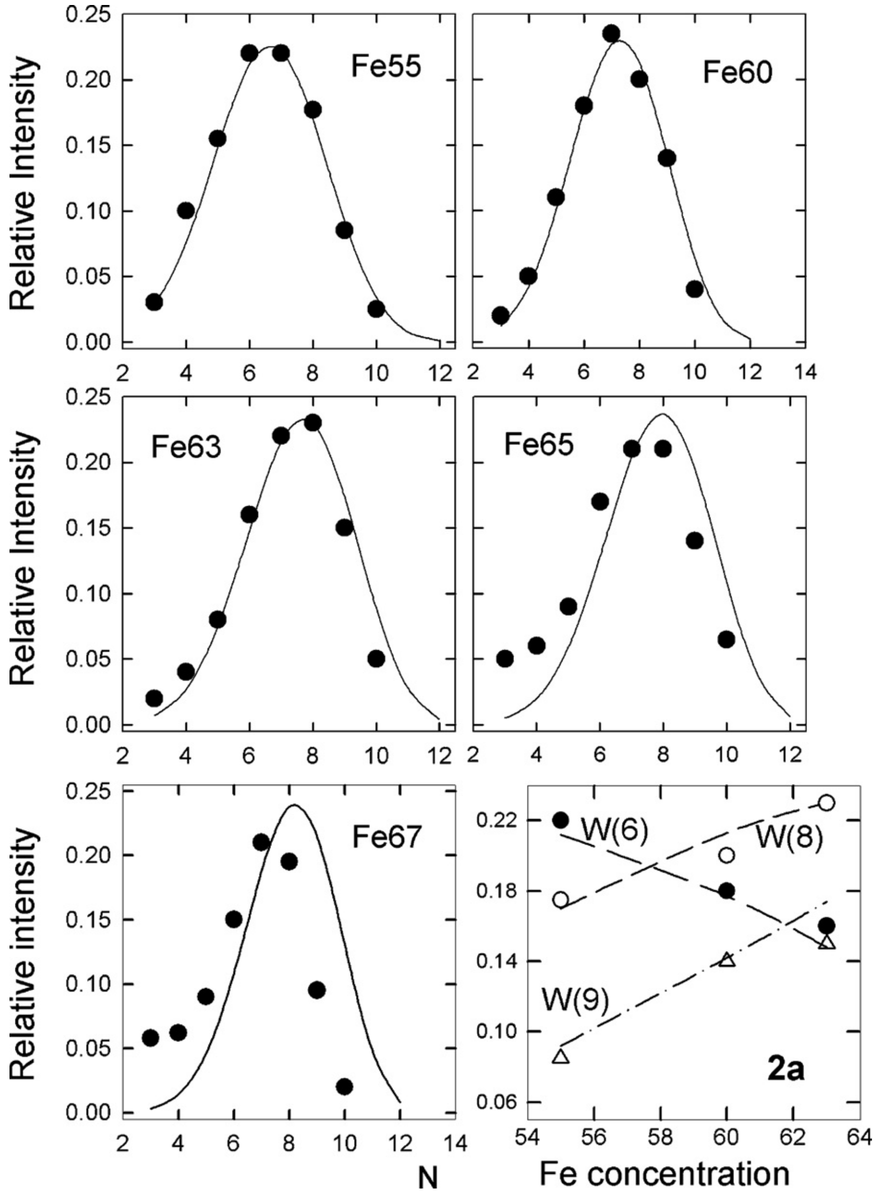

Fig. 2. The comparison of the measured intensities of ferromagnetic components of the main maximum of HFD (closed circles) with the binomial distribution (solid lines). *N* is a number of the Fe atoms in the nearest environment of the central Fe atom. In (a) the composition dependences of the relative intensities of three subspectra with B_{hf} = 36.6 T (triangles), 35.5 T (open circles) and 32.9 T (closed circles) in comparison to the binomial distribution W(*N*) (*N* = 9, 8 and 6, respectively) are shown.

close to the results of the previous measurements [10]. Within the limits of experimental error, any dependence of the IS value on both the composition and the type atomic configuration has not been observed. This means that the replacement of Fe by Ni does not affect the locale electron density at Fe sites appreciably.

3.2. *Low-field components*

Up to now, little attention has given to the LF component of HFD what may be associated directly with the local effects in the Invar problem. Apparently, this is due to the fact that the mechanism of the Invar effect has not been considered as a local one. Moreover, the study of the LF component involves some difficulties arising from its rather small intensity as well as from the partial overlap with the much more intensive lines of the spectra. In our study, these difficulties have been reduced to a certain extent through a resolution enhancement by diminution of the velocity scale factor down to 0.018 mm/s/channel. The LF components are located close to the center of the spectra therefore it can be easily observed in spite of its rather low intensity.

Fig. 3 shows the representative examples of the central part of the Mössbauer spectra measured at 5 K. The LF component is clearly observed. As the Fe concentration increases from Fe60 to Fe63, the intensity of the LF component grows noticeably. Moreover, for the LF component, the IS value differs distinctly from that for the ferromagnetic components of MM. The best approximations of the spectra were obtained when the fitting of LF component was performed with two magnetic subspectra. This well corresponds to the shape profile of the LF component obtained as a result of HFD calculation (see Fig. 1). The results of the fittings are shown in Fig. 3. The measured magnetic hyperfine fields, 1.4(1) and 2.5(1) T, are rather small. (Below we shall abbreviate these two LF subspectra by the LF1 and LF2 components.) The main parameters of two LF components measured at 5 K are listed in Table 2. For both LF components, the IS values 0.37(3) and 0.39(3) mm/s (uncorrected for the second order Doppler shift) are nearly the same. These

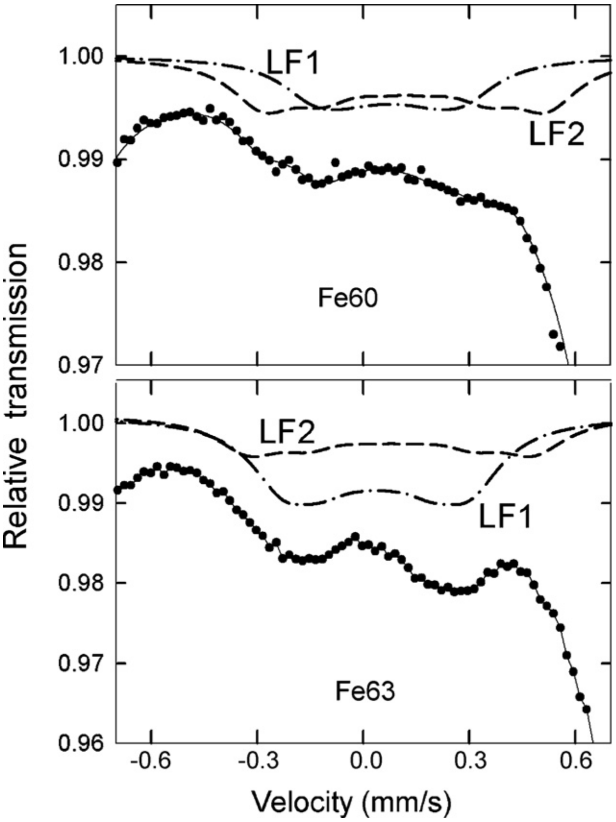

Fig. 3. The central part of the Mössbauer spectra of the Fe60 and Fe63 alloys measured at 5 K. The dashed and dash-dotted lines represent the results of a least-squares fit of the LF component by a superposition of two magnetic subspectra.

values significantly exceed the IS value of the ferromagnetic components of HFD (IS = 0.15 mm/s). For 14.4-keV Mössbauer line of ^{57}Fe isotope, an increase in the IS value implies a decrease in the local electron density. The relative intensities of the LF components as a function of the iron concentration are shown in Fig. 4. The integrated intensity of the LF components increases noticeable with increasing the iron concentration from Fe60 to Fe63. As the iron concentration increases further, the integrated intensity remains nearly unchanged. At the same time, the intensity of the LF2 component increases monotonically closely following the W(11) component of the binomial distribution.

4. Discussion

The quantitative analysis of the experimental data strongly supports that the ground state of the Fe–Ni Invar alloys is predominantly a ferromagnetic state with well-defined local magnetic moments, which are essentially independent of the type of the atomic configuration. For the atomic configurations comprising MM, the B_{hf} values are in well concordance with a simple model based on the direct relationship between the B_{hf} value and the number of Fe atoms in the nearest environment of the central Fe atom. No explicit indication on the non-collinearity of the magnetic moments is found. The constancy of the IS value for the magnetic subspectra of MM suggests that the Fe atoms are in single high-moment electron state. This means that, in the ground state of the Fe–Ni Invar, the ferromagnetic Fe–Ni and Ni–Ni exchange bonds are strongly dominant and the simple ferromagnetic structure of the alloys is not disturbed by the more weak antiferromagnetic Fe–Fe bonds.

Table 2
Parameters of the LF components of HFD at 5 K. The magnetic hyperfine fields (B_{hf}), relative intensities (INT) and isomer shifts (IS) were obtained by fitting LF component by two magnetic subspectra (LF1 and LF2 components). Isomer shifts are given relative to α-Fe at room temperature.

Alloy	LF1			LF2		
	B_{hf} (T)	INT	IS (mm/s)	B_{hf} (T)	INT	IS (mm/s)
Fe55	1.45(9)	0.018(5)	0.35(1)	2.42(12)	0.007(5)	0.40(2)
Fe60	1.36(9)	0.022(8)	0.37(2)	2.50(8)	0.015(6)	0.42(1)
Fe63	1.55(8)	0.034(8)	0.34(2)	2.57(14)	0.026(7)	0.38(2)
Fe65	1.41(7)	0.021(7)	0.39(1)	2.60(6)	0.035(7)	0.37(2)
Fe67	1.38(8)	0.015(5)	0.40(2)	2.43(9)	0.039(6)	0.38(2)

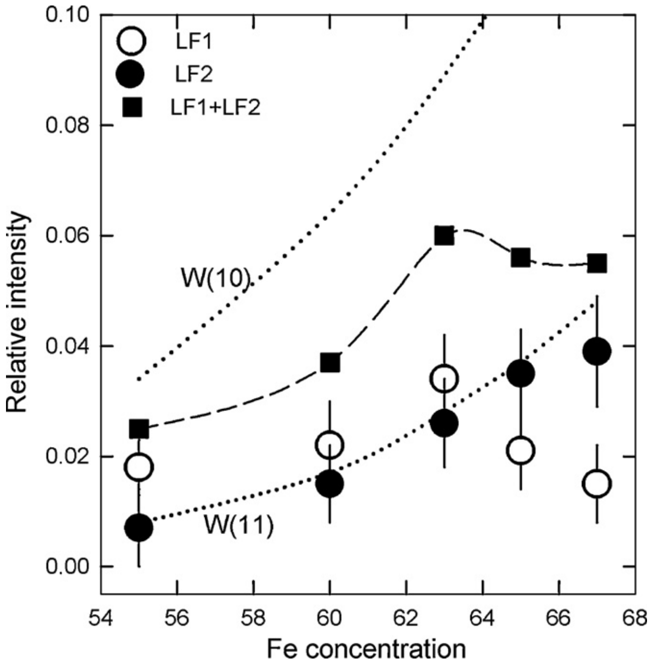

Fig. 4. The composition dependences of the LF components at 5 K. Open and closed circles represent the LF1 and LF2 components, respectively; closed squares show the integrated intensity of the LF component. (Dashed line is a guide to the eye.) The dotted lines are the W(10) and W(11) components of the binomial distribution.

This picture is seems reliable for the atomic configurations for which the number of the Fe nearest neighboring (NN) atoms is not too large ($N < 10$). In the same time, the next peculiarities indicating on the some deviations from this simple picture are observed: (1) the subspectrum $N = 11$ has not been observed. For the Fe65 alloys, as an example, the W(11) probability is equal about 0.04. A subspectrum of such intensity would be detected in our measurements. (2) The observed intensities of the $N = 10$ subspectra are systematically lower as compared to the W(10) probability. (3) For the iron concentrations exceeding 63 at.%, an essential shift of the HFD with respect to the W(N) distribution is observed. This shift is negligible for Fe55 and Fe60 alloys but quite large for Fe67 alloy. These observations give clear evidence that the magnetic states of the central atoms in the atomic configurations $N = 10$ and $N = 11$ are highly unstable.

The self-consistent explanation of these peculiarities may be given with the theoretical predictions concerning the conditions of the formation of the antiferromagnetic (AFM) states of the Fe atoms in the Fe–Ni Invar alloys. As the N number increases, the number of the AFM Fe–Fe pairs increases too. When the number of these AFM pairs reaches some critical value, the AFM alignment of the magnetic moment of the central Fe atom becomes energetically most favorable. Theoretical models [4,8,9] predict that the Fe site, having in its nearest neighborhood 10 or more Fe atoms, will transform into the AFM state with a moment direction antiparallel to the net magnetization. Our experimental results are in well concordance with this prediction. For the explanation of above mention peculiarities (1) and (2), one ought to propose that the moment of the central Fe atom in the $N = 11$ atomic configuration is always antiferromagnetically alignment while the $N = 10$ configurations only partially transform into the AFM state. In latter case, the probability of the forming of the stable AFM state is strongly influenced by the conditions in the neighborhood of the sites. In terms of this picture, the peculiarity (3) can be easily explained too. The observed shifts of HFD with respect to the W(N) distribution arise from the appearance of the AFM sites in the nearest neighborhood of the central Fe atom. According to Eq. (1), one NN Fe atom having the AFM orientation of its moment leads to the reduction of the B_{hf} value to about 3.5 T. The natural consequence of this reduction is the visible increase in the intensity of the low-field part of MM. A simple estimation shows that, for the explanation of the observed shifts of HFD, the net concentration of the AFM sites of several percents is quite enough.

The presence of the AFM Fe sites may be states from the B_{hf} values. If the magnetic moment of the central Fe atom is aligned antiferromagnetically with respect to the neighboring moments, the B_{hf} value at the central Fe atom will be very small. In terms of Eq. (1), in this case, two contributions to B_{hf} (one due to the magnetic moment of the central atom, the other due to the neighbor magnetic atoms) have opposite signs and nearly cancel each other. As a result, B_{hf} at the central Fe atom is reduced down to several Tesla. This is well agrees with the B_{hf} values observed for the LF components. The predicted theoretically concentration of the AFM sites is very close to the observed relative intensity of the LF component. Thus, the proposition that the LF component corresponds to the Fe sites with the AFM alignment of the magnetic moment seems to be highly probable.

The most prominent feature of the LF component is the anomalous IS value which is essentially larger than the IS value of the ferromagnetic component of HFD. The experimental data show that the local electron density at the LF-sites is much smaller than at ferromagnetic ones. Basically, two different reasons for the change in the electron density may be considered: a change of the electron structure of the Fe atom and a local change of the atomic volume. From the quantitative analysis of the data on the ^{57}Fe IS for the Fe impurity atoms in the transition metals [18] it is evident that the first cause may have only slight effect on the electron density. However, it is not easy to predict the changes in the local electron density when the transition from ferromagnetic state to AFM state is occurs. In order to consider the dependence of IS on the atomic volume, we can use data on the IS in different transition metals as a function of pressure [19]. It has been shown that a simple scaling interrelation exists between the IS value and the volume. Namely, as a first approximation, the logarithmic derivative $\partial \mathrm{IS}/\partial \ln V$ is close to 1 mm/s. This means that the 1% change in volume leads to the 0.01 mm/s change in the IS. Within the framework of this approximation, let us assume that the difference in the IS between AFM sites and ferromagnetic ones is completely determined by the change in the volume. Then, we found that the local atomic volume of the AFM site is about 20% greater then the atomic volume of the ferromagnetic configurations. This corresponds to the increase in the interatomic distances by about 7%. This value might appear to be unrealistically large, although the first-principles theoretical analysis of the atomic displacements in the Fe–Ni Invar alloys showed [17] that the dispersion of Fe–Fe nearest neighbor bond lengths can be even greater, up to 9%. Of course, the above-derived estimation of the change in the atomic volume does not claim to the quantitative consistency with the real situation. Nevertheless, it may be proposed that the volume effect is one of the plausible reasons for the increase in the IS value for LF components. In this case, we should suggest that the formation of the AFM sites leads to an increase in the local atomic volume. In terms of this assumption, a simple physical interpretation may be given to the observed features of the LF components of HFD.

The properties of the Invar alloys are largely determined by a competition between the AFM exchange Fe–Fe interaction and ferromagnetic interactions Fe–Ni and Ni–Ni. The strength of the AFM exchange is much smaller than that of ferromagnetic interaction; however, this is compensated partly by a large number of the Fe–Fe bonds. The magnetic state of the Fe atom as well as the interatomic distances should depend on the balance between the exchange interactions opposite in sign. The most important factors determining the ground-state properties of the Invar alloys are the radial dependences of the exchange interactions between different types of atoms. Unfortunately, this information is lacking completely at the moment. Therefore, the qualitative examination of the picture is only available.

In accordance with the accepted picture, the intensity of the LF component is determined by the atomic configurations in which the central Fe atom has 10 and 11 NN Fe atoms. (A contribution from the configuration with 12 NN Fe neighbors is rather small and can be neglected.) For these AFM configurations, all the Fe–Fe exchange bonds are energetically satisfied whereas the ferromagnetic Fe–Ni bonds are not satisfied because the magnetic moment of the central Fe atom is antiparallel to the moments of the neighboring Ni atoms. The energetically most favorable state is one in which the contribution of the unsatisfied Fe–Ni bonds to the total energy is minimal. As seen in Fig. 4, the relative intensity of the LF2 component as a function of composition follows closely the W(11) probability of the binomial distribution. This result allows us to conclude that the LF2 component corresponds to the AFM Fe atoms having 11 Fe atoms in its nearest neighborhood. Then, the LF1 component should correspond to the configuration with 10 NN Fe atoms. However, as is seen in Fig. 4, the observed intensity of the LF1 component is significantly less as compared with the W(10) probability. This means that the 10 NN configurations only partially transform into the AFM states. The integrated intensity of the LF component is only a weak function of on the composition reaching a plateau over Fe63 (see Fig. 4). Such a behavior of the integrated intensity can be realized if take into consideration the local distortions of the lattice caused by the increase in atomic volume of the AFM Fe sites. From stability of the lattice considerations, it is evident that the full concentration of such sites cannot be large. The experimental results show that the maximal concentration of the AFM Fe atoms is close to 6%. Thus, the proposed scenario provides a qualitative explanation for the experimentally observed regularities. In framework of this picture, from our experimental data it follows that, for the AFM Fe states, an increase in the atomic volume is needed to fulfill the requirement of the minimization of the contribution of the unsatisfied Fe–Ni bonds to the total energy. The LF atomic configurations which considered as the AFM ones have larger locale atomic volume as compared with the ferromagnetic configurations consisting MM of HFD.

This conclusion is in a contradiction with the ordinary theoretical results which suggest that the AFM states of the Fe atoms should have a smaller volume (see [8,17] and references herein). However, it should be noted that the theoretical suggestion has never been confirmed by direct experiments. As have already been mentioned, the magnetic state of the Fe atom as well as the atomic volume are determined by a delicate balance between the competitive contributions of the energetically satisfied and unsatisfied exchange bonds to the total energy. For correct analysis of the balance, the reliable information on the radial dependencies of the exchange interactions between different atoms is required. Unfortunately, this information is lacking. Taking into account the radial dependence of non-satisfied Fe–Ni interaction seems to be particularly important. In fact, the dependence of the magnetic state of the Fe atoms on the relationship between the radial dependences of different exchange bonds has never been considered. Sometime it is proposed even that the ferromagnetic Fe–Ni and Ni–Ni interactions do not depend on the interatomic separations on the whole [9]. It is obvious that this assumption should not be correct. Theoretic models predict also that the formation of the AFM states in the Fe–Ni Invar should be associated with a loss of local moment magnitude. Experimentally, this prediction has not been directly confirmed. Our interpretation of the feature of the LF components of HFD is quite plausible although the direct proof of the AFM character of that state is absent. Therefore, the relationship between the magnetic state of the Fe atom and local atomic volume remains open to question. An unambiguous answer on the problem will be rather important for understanding of the role of the local effect in the origin of the Invar effect. In order to obtain deeper insight into this phenomenon, the further experimental and theoretical efforts will be required.

5. Conclusions

In summary, we have studied the features of the hyperfine field distribution of the Fe–Ni Invar alloys in the concentration range of 55–67 at.% Fe. The careful investigation on the concentration dependencies of the parameters of the Mössbauer spectra has been performed at 5 K. As a result, the reliable data on the correspondence between the B_{hf} magnitude and the type of the locale atomic configuration were obtained. It is confirmed that the Fe–Ni Invar alloys in their ground state are predominantly collinear ferromagnets with the well-defined atomic magnetic moments. Particular emphasis has been placed on the LF component of the distribution, which exhibits some anomalous properties. We argue that the LF component corresponds to the Fe atoms having the AFM alignment of its magnetic moment. The most striking feature of the LF component is the large positive isomer shift exceeding by about 0.2 mm/s the value of the isomer shift for the main (ferromagnetic) components. The corresponding reduction of the local electron density may come at last partly from an increase in the atomic volume. The local increase in the atomic volume is a consequence of a competition between energetically satisfied and unsatisfied bonds on the Fe sites having 10 or more Fe nearest neighbors. This interpretation is in well accordance with the observed concentration dependences of the parameters of the LF components. The magnitudes of B_{hf} and the relative intensities of the LF components support this assumption also. Because the direct proof of the AFM character of the LF-sites is absent, the further experimental and theoretical efforts will be required. The direct examination of the existence of the AFM states, in principal, could be made by neutron diffraction technique; however very accurate measurements are required because the fraction of the LF (AFM) sites do not exceed 6%. The theoretical analysis of stability of the AFM states with use correct hypothesis on the radial dependences of the exchange interactions between different atoms is highly desirable also. Our studies on Fe–Ni Invar alloys at the temperatures above 5 K are now in progress. It is quite possible that the phenomena observed in our experiment are closely related to the discovery of the elastic diffuse scattering of neutrons, which was explained by the formation of microclusters with a locale lattice deformation [16]. The results indicate that the Fe-rich clusters have expanding volume at low temperature.

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