

The Mössbauer effect and magnetic structure of an Invar alloy with manganese impurity

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The temperature dependence of the Mössbauer effect and of the magnetization of iron-nickel Invar containing manganese as an impurity is studied from 4.2°K up to the Curie point. A joint analysis of the magnetization and of the Mössbauer spectra shows that the magnetic moment of the iron depends only on the number of nickel atoms among its nearest neighbors. This dependence has been determined quantitatively for the first time. It is suggested that the magnetic-moment values obtained for the iron are universally valid for face-centered cubic iron-nickel alloys.

Invars are usually defined as fcc alloys of the Fe-Ni system containing (28-40) at.% Ni. The physical properties of these alloys have a large number of singularities. These include the temperature behavior of the expansion coefficient and of the elastic moduli, a strong dependence of the Curie temperature (T_C) on the composition, high magnetic susceptibility and magnetostriction of the para-process, etc. The physical nature of the singularities is still unclear, although all the available data point to a close connection between the anomalies and the magnetic state of the alloy. Recently, invar models have appeared^[1-4], based on allowance for the inhomogeneities of the magnetic structure. However, the properties of the magnetic inhomogeneities have not been sufficiently well investigated experimentally. It is therefore promising to use for invars Mössbauer spectroscopy supplemented by measurements of the macroscopic magnetic moment.

We have investigated the temperature dependences of the Mössbauer effect and of the magnetization of an invar alloy with Mn impurity. A small amount of Mn was added to the invar Fe-32Ni in order to lower the temperature of the martensitic transition to the bcc phase. It is assumed that this increment does not influence the magnetic structure, so that the alloy retains the invar anomalies. Indeed, according to our data, the decrease of T_C relative to the Fe-32Ni alloy is only 12°. At 130°K, a martensitic transformation begins in the Fe-32Ni alloy, and in the investigated alloy this transition was not observed even at 4.2°K.

1. SAMPLES AND MEASUREMENT PROCEDURE

The chemical analysis of the pre-homogenized alloy has shown that it contains 67.2, 31.8, 0.8, and 0.2 at.% of Fe, Ni, Mn, and Si; the other impurities did not exceed 0.02; the Si is a technological additive and also lowers the martensitic temperature.

The samples for the magnetic measurements were cut out from a ribbon 1 mm thick, using a template in the form of an ellipse with axes 35 and 3 mm. For the Mössbauer measurements we used foils 0.025 mm thick. All the samples were soaked at 1000°C for two hours and quenched in water. The magnetic measurements were made at temperatures 220-420°K in a magnetic field 200 Oe by a ballistic method. The Mössbauer spectra were registered in the interval 4.2-450°K with a spectrometer of the electrodynamic type, with an AI-256 analyzer and with a Co⁵⁷ (Pd) source at room temperature. The temperature T_C of the alloy was determined from the temperature dependence of the magnetization, and also from the start of the broadening of the paramagnetic Mössbauer spectrum. Both methods yielded identical results: $T_C = 413 \pm 2^\circ\text{K}$.

2. EXPERIMENTAL RESULTS AND DISCUSSION

1. Magnetization. The relative values of the magnetization σ as a function of the relative temperature $\tau = T/T_C$ are shown in Fig. 1a (dark circles). The solid line in Fig. 1a represents σ calculated by the theory of the local molecular field. The magnetization at 0°K, relative to which the experimental values are given, was also obtained by calculation and was equal to 125 emu/g.

According to the theory, the time-averaged value of the z-projection of the atomic magnetic moment is determined by the body bonds with their neighbors, within the limits of several coordination spheres. Tomiyoshi, Yamamoto, and Wanatabe^[5] pointed out that the exchange in invars is short-range, and presented a qualitative picture of the molecular fields. Natta and Billard^[6] have succeeded in describing the magnetization of the invar alloys with the aid of band theory, using a cell of 13 atoms as a basis. In this paper we consider localized

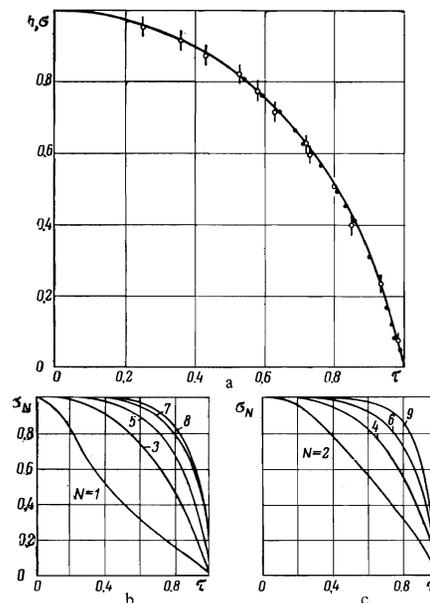


FIG. 1. a) Dependence of the relative magnetization σ and of the relative effective field $h = \bar{H}_{\text{eff}}/\bar{H}_{\text{eff}}^0$ on the relative temperature $\tau = T/T_C$ ($T_C = 413^\circ\text{K}$). The black circles show the experimental values of the magnetization. The solid curve is the plot of σ calculated by the theory of the local molecular field. The light circles show the values of h from the Mössbauer spectra. $\bar{H}_{\text{eff}}^0 = 280$ kOe is the average effective field at 4.2°K. b, c) Illustration of the molecular-field approximation. The σ_N curves show the relative temperature dependence of the z-projection of the magnetic field of the atom whose exchange bonds extend only to N out of the nearest 12 neighbors.

moments, the interaction of which is confined to the first coordination sphere. In the calculation of σ it is assumed that each lattice site corresponds to a magnetic moment (μ) that coincides with the average magnetic moment of the alloy at 0°K. The exchange integral between atoms located in a given site and its nearest neighbors was assumed to be equal to NJ . Here $J > 0$, and N is the actual number of Fe atoms in the surrounding of the considered site. This form of exchange integral is connected with the fact that in the fcc Fe-Ni alloys the exchange integral of the atom pair Fe-Fe is assumed to be very small in comparison with the integral for the Fe-Ni and Ni-Ni pairs.

For the molecular field at the selected site we can write

$$H(N) = \frac{2}{g\mu_B} NJ\bar{S}, \quad (1)$$

where $g\mu_B\bar{S}_Z = \mu_Z$; $H(N)$ is connected with $S_Z(N)$ with the aid of the general molecular-field relation

$$S_i(N) = SB_s \left(\frac{g\mu_B SH(N)}{kT} \right). \quad (2)$$

Here g is the Landé factor, μ_B is the Bohr magneton, k is Boltzmann's constant, and $B_S(y)$ is the Brillouin function corresponding to the spin S .

It is convenient to rewrite relations (1) and (2) in relative form, introducing

$$\sigma_N = S_i(N)/S, \quad \sigma = \bar{S}_i/S, \quad \tau = \frac{3kT}{2S(S+1)}(J\bar{N})^{-1}.$$

We then obtain

$$\sigma_N = B_s \left(\frac{3S\sigma N}{(S+1)\tau\bar{N}} \right), \quad (3)$$

where $\bar{N} = 12c$ and c is the atomic concentration of the Ni in the alloy. On the other hand

$$\sigma = \sum_{N=0}^{12} p(N)\sigma_N, \quad (4)$$

where $p(N)$ is the probability of finding N nickel atoms among the nearest neighbors of the selected lattice site. For a disordered alloy we have

$$p(N) = \frac{12!}{N!(12-N)!} c^N (1-c)^{12-N}. \quad (5)$$

A simultaneous solution of (3) and (4) was obtained by successive approximations and is shown by the solid curve of Fig. 1a at $g = 2$ and $S = 3/2$. The σ_N curves for different N are shown in Figs. 1b and c, while the values of $p(N)$ are listed in the table.

The described model contains only one T_C for the entire alloy, with the exception of the configurations with $N = 0$, which will be paramagnetic. The question

of the real magnetic order in these configurations remains open, since the alloy always contains long-range interactions that can lead to magnetic ordering. Although they are much weaker than the interactions between the nearest neighbors, they are capable of influencing T_C and σ_N . On the basis of the results of Coey and Sawatzky^[7], it can be assumed that significant deviations appear only for $N = 0$. However, the contribution of these configurations to the magnetization of the investigated alloy is small and can be neglected.

2. Mössbauer effect. The Mössbauer effect at Fe⁵⁷ in invars was investigated in detail recently in^[4, 5, 6] A broad distribution of the effective hyperfine fields was observed, and was found to depend strongly on the concentration and on the temperature. The average effective field (\bar{H}_{eff}) is proportional here to the magnetization. In the analysis of the spectra in these studies, no account was taken of the dynamic correlations of the magnetic moments, which is essentially equivalent to introduction of molecular fields. In this case, the set of H_{eff} reflects the corresponding distribution of the z -projections of the magnetic moment of the Fe atom (μ_{Fe}) in the alloy, due to the fluctuations of the molecular field and to the possible dependence of μ_{Fe} on the atomic surrounding. It is extremely difficult to separate the two contributions by using only the Mössbauer spectra, although this question is of great interest for the theory of invar anomalies. Another important problem in the interpretation of the spectra is the very possibility of neglecting the correlations of the moments. Indeed, since the averaging time of the hyperfine interactions in the Mössbauer effect amounts to only $1/\omega_L \approx 10^{-8}$ sec, it follows that the correlations can appear in the spectra and produce specific relaxation effects. Here ω_L is the Larmor precession frequency of the nuclear moment in the field \bar{H}_{eff} at 0°K. Moreover, the relaxation effects explain quite well certain singularities of the spectra of Invars, as first pointed out by van der Woude and Dekker^[9]. In our case, an attempt to solve these problems is made easier by the fact that if μ_{Fe} does not depend on the surrounding, then the fluctuations of the molecular fields can be determined from magnetization measurements. The experimental spectra and the spectra corresponding to the μ_{Fe} z -projection distribution connected with the molecular fields only, are shown in Figs. 2 and 3 for 4.2 and 300°K, respectively. To construct the spectra we used lines of Lorentz shape with a paramagnetic-spectrum width 0.49 mm/sec and an intensity ratio 3:2.3:1. At a fixed temperature, the calculated spectrum is a superposition of 12 effective fields. It was assumed that $H_{\text{eff}}(N) = \bar{H}_{\text{eff}}^{(0)}\sigma_N$. The total area of the lines with given $H_{\text{eff}}(N)$ is proportional to $p(N)$, and their center of gravity does not depend on N . At 4.2°K the average effective field is $\bar{H}_{\text{eff}}^{(0)} = 280 \pm 10$ kOe. The method of calculating $\bar{H}_{\text{eff}}^{(0)}$ will be considered below. In the calculation of the model spectra, we took into account the line broadening due to the difference between the molecular fields at the nearest neighbors of the selected Fe atom. The molecular field at these atoms are not equal to the average field in the alloy, as would follow from formula (1), but depend on the exchange bonds with their neighbors in the lattice. The relative broadening is given by the formula^[7]

$$\Delta\Gamma = \frac{6\gamma S}{(S+1)\bar{N}\tau} \frac{dB_s}{dy} \sqrt{\left\{ 12 \sum_{N=1}^{12} p(N) [\sigma_N - \sigma]^2 \right\}}; \quad (6)$$

where $\gamma = 1$ for lines 1 and 6, 0.579 for lines 2 and 5, and 0.157 for lines 3 and 4. The value of $\Delta\Gamma$ is negli-

N	$p(N)$, %	Relative areas of components, %	$[\mu_{\text{Fe}}(N) \pm 0.2], \mu_B$
0	1.0	2 ± 2 (P_0)	-0.4
1	5.5	8 ± 3 (P_1)	0.2
2	14.2	13 ± 2 (P_2)	1.3
3	22.4	21 ± 2 (P_3)	1.8
4	23.7		2.1
5	17.9		2.2
6	9.8		2.2
7	4.0	55 ± 1 (P_4)	2.2
8	1.1		2.2
9-12	<0.5		2.2

Note. The values of $\mu_{\text{Fe}}(N)$ were obtained with the aid of formula (8) from the values of $H_{\text{eff}}(N)$ determined from the Mössbauer spectra, using the following parameters in (8): $A = 120$ kOe/ μ_B ; $B = 50$ kOe/ μ_B , $\mu = 1.4 \mu_B$. The value of $H_{\text{eff}}(N)$ at $N \leq 5$ was taken from Fig. 4. At $5 < N < 12$ we have $H_{\text{eff}}(N) = H_{\text{eff}}(5)$.

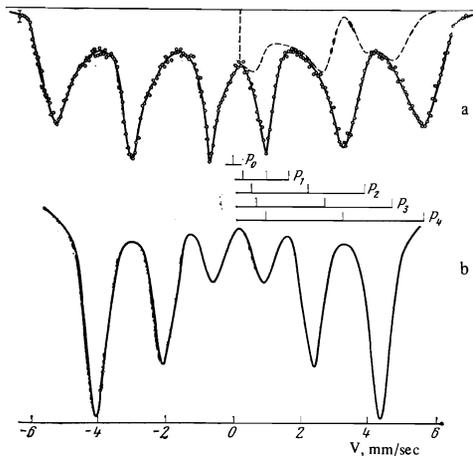


FIG. 2. Experimental (a) and model (b) Mössbauer spectra at 4.2°K. The solid line (a) represents visual averaging of the experimental points. P_0 to P_4 are the components of the spectrum. Each component, except P_0 , is represented in the spectrum by six lines. The positions of the lines 4, 5, and 6 are indicated by the vertical strokes. The dashed lines show the part of the spectrum remaining after subtracting lines 4-6 of the component P_4 . The method of calculating the model spectrum is explained in the text. Zero velocity is taken to be the center of gravity of the spectrum of pure Fe at 300°K.

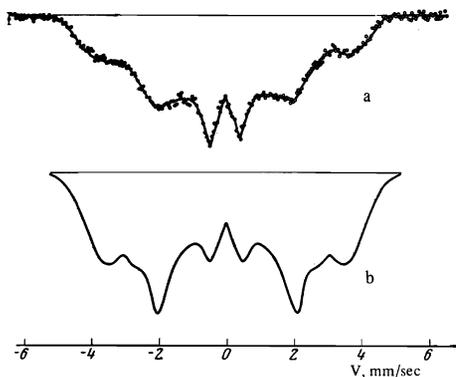


FIG. 3. Experimental (a) and model (b) Mössbauer spectra at 300°K. The method of constructing the model spectrum is explained in the text. The solid line (a) represents freehand averaging of the points. Zero velocity is taken to be the position of the center of gravity of the spectrum of pure Fe at 300°K.

gibly small at 4.2°K and reaches 0.2–0.3 at 300°K. As seen from Figs. 2 and 3, there is a significant difference between the experimental and model spectra in the line widths in the H_{eff} range. In the experimental spectra, the lines are approximately twice as broad and much larger set of H_{eff} is represented than in the model spectra. Further analysis of the spectra was carried out under the assumption that the line broadening in the spectra is connected with relaxation, and the set of H_{eff} was determined by the dependence of μ_{Fe} on the composition of the atomic surrounding in the first coordination sphere.

The influence of spin correlation on the Mössbauer spectra of magnetically ordered systems was considered by Levinson and Luban in [10]. They have shown that one should expect line broadening even in the case when the characteristic correlation type (t_c) is shorter than $1/\omega_L$, and in the simplest cases the broadening is quadratic in γ . The condition $t_c < 1/\omega_L$ is necessary for the proportionality of the average \bar{H}_{eff} to the magnetization. The spectrum of Fig. 2a has a complicated shape. It can be regarded as a sum of several components, each represented by six lines and characterized by its own value of H_{eff} . In the spectrum of Fig. 2a, the first and sixth

lines of the most intense component with $H_{\text{eff}} \approx 332$ kOe are distinctly pronounced, so that these lines can be easily separated from the spectrum. It turns out that the shapes of these lines are well described by the expression

$$\varphi(x) = \frac{C}{1+0,75(x/\Gamma)^2+0,25(x/\Gamma)^4}, \quad (7)$$

C is a constant, Γ is the total width at half height, and x is the distance from the line center. Expression (7) was first proposed by Shirane [11]. We have postulated this shape for all the lines of the spectral components. Using formula (7) and assuming that $\Delta\Gamma \sim \gamma^2$, we can calculate all six lines of the component with $H_{\text{eff}} \sim 332$ kOe and subtract it from the experimental spectrum. The part of the spectrum shown after subtracting 4–6 lines is shown by the dashed line in Fig. 2a. A successive application of this procedure has made it possible to resolve the experimental spectrum into four components (P_1 – P_4) and a single line (P_0). The relative areas of P_0 – P_4 are given in the table, and the values of H_{eff} and the positions of the center of gravity (δ) are shown in Fig. 4. The errors in the table and in Fig. 4 are the deviations from the mean, obtained by an independent reduction of the right-hand and left-hand halves of a number of spectra. When the spectrum was resolved, the only free parameter was the ratio of the values of C for the lines corresponding to the individual components. The best values of C were those for which the areas of the pairwise identical lines had a ratio 3:2.3:1. This result agrees with [8], in which the spectra were resolved into Lorentz lines of equal width and the same ratio was obtained for their intensities.

The spectra measured at different temperatures were similarly resolved, and the dependence of the relative H_{eff} on τ was determined. It is shown in Fig. 1a (light circles). We note that the accuracy of the resolution is greatly decreased with increasing measurement temperature.

It is seen from the table that the areas of P_0 to P_3 are close to the corresponding $p(N)$, with $N = 0$ and 1 to 3, while the area of the component P_4 is equal to $\sum p(N)$ at $N = 4$ to 8. Since the investigated alloy is disordered, the agreement between the areas and $p(N)$ demonstrates the correctness of the resolution of the spectrum. This fact is also important because it makes it possible to interpret the Mössbauer spectra on the basis of the properties of the local surroundings of the Fe atoms. Therefore the values of $H_{\text{eff}}(N)$ for components obtained from the resolution are shown in Fig. 4 as functions of the number of Ni atoms in the Fe surrounding. For a single line, $H_{\text{eff}} \approx 20$ kOe. The value $H_{\text{eff}} \approx 332$ kOe corresponds to P_4 and represents the average value

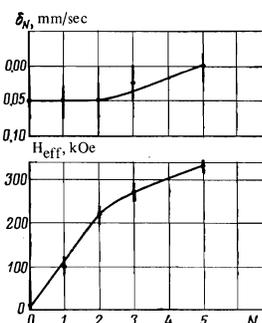


FIG. 4. Position of the center of gravity δ of the Mössbauer spectrum and the effective hyperfine field (H_{eff}) for the Fe atoms as a function of the number N of the Ni atoms in the nearest surrounding.

of H_{eff} for the Fe atoms surrounding more than three Ni atoms. For the investigated Ni concentration, this H_{eff} corresponds to $N \approx 5$. The differences between $H_{\text{eff}}(N)$ and $H_{\text{eff}}(5)$ at $4 \leq N \leq 8$ are small and do not exceed the average width of the first and sixth lines of the components P_4 , which amounts to ~ 30 kOe.

The values of δ_N are shown in Fig. 4 relative to δ_5 . The general course of δ_N reflects adequately the spectrum asymmetry observed in Figs. 2a and 3a.

As is well known, $H_{\text{eff}}(N)$ can be approximately represented in the form

$$H_{\text{eff}}(N) = A\mu_{\text{Fe}}(N) + B\mu. \quad (8)$$

Here A and B are constants, the first term in the right-hand side is due to the polarization of the ion core of the Fe atom, while the second term represents the contribution made to H_{eff} by the polarized conduction electrons and is proportional to the average magnetic moment per atom of the alloy. It can thus be shown that the rapid decrease of $H_{\text{eff}}(N)$ at $N < 4$ is due to the decrease of μ_{Fe} , whereas at $4 \leq N \leq 8$ the value of μ_{Fe} is practically independent of N. The last statement agrees well with the measurements of μ_{Fe} in Fe-Ni alloys with large Ni content ($c > 0.5$), in which the principal configurations are those with $N > 4$. It has been established for these alloys that μ_{Fe} does not depend on the Ni concentration, and that μ_{Fe} obtained from Eq. (8) is equal to $\approx 2.2 \mu_{\text{B}}$. It is therefore reasonable to assume that in the entire range of fcc Fe-Ni alloys the value of μ_{Fe} is determined only by the parameter N. Naturally, $H_{\text{eff}}(N)$ will depend additionally on the actual content of the Ni in the alloy. In this approximation it is possible to determine $\mu_{\text{Fe}}(N)$ quantitatively for invar from Eq. (8) after first obtaining A and B from the known values of μ_{Fe} and μ_{Ni} , and from the average \bar{H}_{eff} in the concentration region $c > 0.5$. The value \bar{H}_{eff} at 4.2°K decreases linearly from 335 kOe for $c = 0.5$ to 280 kOe for $c = 1.0$. The corresponding change of μ is from 1.7 to 0.6 μ_{B} . \bar{H}_{eff} for $c = 0.5$ was obtained in our measurements, and for $c = 1.0$ it was taken from^[12]. Then $B = 50$ kOe/ μ_{B} , and the value $A = 120$ kOe/ μ_{B} was determined by Wertheim^[13]. Using these constants and assuming that $\mu_{\text{Ni}} = 0.6 \mu_{\text{B}}$ for the entire fcc region, we can find μ for the magnetic saturation of the investigated alloy from $\bar{H}_{\text{eff}} = 280$ kOe. The value $\mu = 1.4 \mu_{\text{B}}$ agrees with the magnetic measurements of Shiga^[14]. The values of $\mu_{\text{Fe}}(N)$ calculated in this manner from $H_{\text{eff}}(N)$ are listed in the table. The minus sign for $\mu_{\text{Fe}}(0)$ means that the moment of the Fe atom is directed opposite to μ . In Subsection 1 of Sec. 2 it was indicated that Fe atoms with $N = 0$ should be paramagnetic. Actually, however, their magnetic moments are "antiferromag-

netically" ordered. This question is of particular interest in connection with theories of antiferromagnetic origin of invar anomalies^[15].

The behavior of $\mu_{\text{Fe}}(N)$ explains the behavior of δ_N . The increase of δ means a decrease of the density of the 4s electrons at the Fe nuclei. According to^[13], at a constant number of 4s electrons in the alloy, the decrease of their density at the Fe nuclei may be due to the increase of the screening by the localized 3d electrons that are responsible for the magnetic moment.

3. CONCLUSION

As the result of a study of the magnetization and of the Mössbauer effect in invar, the martensitic point of which is lowered by introducing a small amount of Mn, we observed an inhomogeneous magnetic structure. The magnetization is satisfactorily described by assuming fluctuations of the molecular field. The Mössbauer spectra are not due entirely to these fluctuations, and point to a dependence of the magnetic moment of the iron on the composition of the nearest neighbors. The analysis of the spectra has made it possible to obtain, for the first time, numerical results for this dependence.

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