Mössbauer investigation of Invar. A new model of the expansion anomaly and magnetism of iron atoms

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An experimental investigation was made of the distribution of the effective fields at the iron nuclei, thermal expansion, and saturation magnetization of Invar (alloy of iron with 36 wt.% of nickel) at various temperatures. A combined analysis of the results made it possible to determine for the first time the dependence of the atomic volume of iron on the effective field at the nuclei, which is a "good" characteristic of the magnetic state of the atoms. This dependence did not fit the existing theories and models of Invar. A new quantitative model was developed for the Invar expansion anomaly in which the exchange polarization of some iron atoms by localized moments of the immediate environment increases correspondingly the atomic volume.

Among the numerous anomalies of the properties of Invar (Fe–36 wt.% Ni) the most characteristic and of the greatest practical importance is the considerable reduction in the thermal expansion in the ferromagnetic state. The "normal" compression of the lattice as a result of cooling below the Curie temperature is compensated by a giant spontaneous magnetostriction. It is well known that the spontaneous magnetostriction of Invar is due to the characteristic features of the magnetic state of the Fe atoms, but a satisfactory microscopic theory is not available. Quantitative semiempirical models of the Invar anomaly[1–3] proposed in recent years are based on the mutually exclusive models of magnetism and, consequently, are not sufficiently convincing. It would therefore be of considerable interest to investigate experimentally the influence of magnetism on the atomic volume which would make it possible to verify the basic assumptions of the existing Invar models and to identify the characteristic features of the magnetism of the Fe atoms which should be allowed for in any theory of the anomalous properties of this alloy.

In the present study the distributions of the effective fields at the Fe nuclei found from the Mössbauer spectra were compared with the magnetostriction values. This yielded the dependence of the atomic volume of Fe on the effective field that represents the magnetic state of the atoms. A simultaneous analysis was made of the temperature dependences of the effective field and saturation magnetization. All the results indicated that the Invar anomaly is due to the appearance of the magnetic moment at the Fe atoms which have no more than three Ni atoms in the immediate environment.

The Mössbauer spectra of Invar were recorded at temperatures 4.2–550 K using a constant-acceleration spectrometer in the absorption geometry with a ^{57}Co(Cr) source. The magnetization was determined employing a vibrating sample magnetometer and the thermal expansion was found with a quartz dilatometer. Samples were in the form of a foil 25 μ thick formed by rolling the Fe–36 wt.% Ni alloy, annealed in vacuum at 1000 °C for 2 h, and quenched in water. All the measurements were made on the same samples. The Mössbauer spectra were analyzed into their components by a method suggested in Ref. 4 and it was found that the ratio of the intensities of the lines in one component was 3:2.3:1 and the line width was 0.3 mm/sec. This intensity ratio was found to fit the results best after various adjustments and the adopted line width corresponded to the spectrum of pure iron of the same thickness as the investigated samples, which were used to calibrate the spectrometer. The spontaneous magnetostriction values were found by subtracting the lattice contribution from the experimental thermal expansion spectrum; this contribution was estimated using the Debye theory and the thermal expansion of Invar in the paramagnetic state and the Debye temperature, taken to be 400 K.

The dependences of the intensities of the components of the Mössbauer spectrum on the effective field $P(H_{\text{eff}})$, representing the probability density of the distribution of H_{eff}, are plotted in Fig. 1 for the temperatures 4.2, 300, and 410 K. These dependences have a complex structure consisting of several maxima. The vertical line in Fig. 1 identifies the position of the main maximum representing the most probable

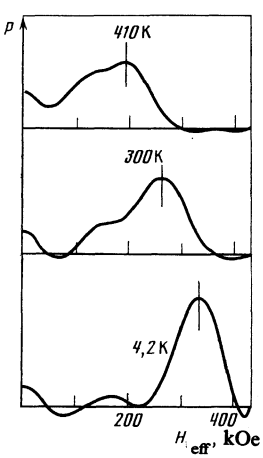

FIG. 1. Distribution of the effective fields in the Mössbauer spectra at different temperatures. The vertical line identifies the position of the most probable field.

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value of H_{eff} in the spectra. We can see that an increase in temperature shifts the main maximum and increases its width, and reduces the total intensity. The presence of the maximum corresponding to the most probable H_{eff}, its shift and expansion without a change in the total intensity, are the usual consequences of thermal fluctuations of the magnetization in Fe–Ni alloys.[5] Therefore, the Invar anomaly sould be due to the Fe atoms which correspond to $P(H_{\text{eff}})$ after subtraction of the main maximum. A redistribution of the intensity in turn means that these Fe atoms are characterized by a much greater change in the magnetic state which is possibly due to a reduction in the magnetic moment. In this situation the Mössbauer spectroscopy method provides a unique opportunity for a quantitative description of the distribution of the magnetic states of the Fe atoms responsible for the Invar anomaly. Without loss of generality, at all temperatures below the Curie point we can assume that

$$\omega_S(T)=c\int p(H,T)\,(\Delta v/v)_H\,dH, \tag{1}$$

where $\omega_S(T)$ are the absolute values of the anomalous compression of Invar found by subtraction of the magnetostriction at 4.2 K from the values at other temperatures. The temperatures dependence $\omega_S(T)$ is represented by the continuous curve in Fig. 2. The function $p(H,T)$ represents $P(H_{\text{eff}})$ at various temperatures after subtraction of the main maximum; $(\Delta v/v)_H$ is the relative change in the atomic volume of iron, understood to be the volume per one atom. The quantity $c=0.65$ is the atomic concentration of iron. The values of $p(H_{\text{eff}})$ were found at ten temperatures and substituted into Eq. (1) where the integral was replaced by a sum. The resultant system of linear equations was solved by the method of least squares[4] for $(\Delta v/v)_H$. This yielded the dependence of $(\Delta v/v)_H$ on H_{eff}. To a good approximation, this dependence was linear:

$$(\Delta v/v)=aH-b. \tag{2}$$

Here, $a=3\times10^{-2}$ (%/kOe) and $b=2\%$. The calculated values of $\omega_S(T)$ are represented by black squares in Fig. 2. Since Eq. (1) was applied for the first time to an analysis of the experimental results, we regarded the agreement between calculated points and the experimental curve as satisfactory.

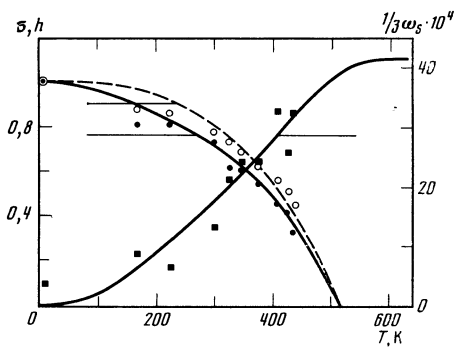

FIG. 2. Anomalous compression of the Invar lattice (ω_S) and the saturation magnetization (σ) plotted as a function of temperature (continuous curves). The calculated values of ω_S (■), of the relative average effective field in the Mössbauer spectra (●), and of the most probable effective field h (○) are shown.

Figure 2 gives the temperature dependences of the relative value of the saturation magnetization σ (continuous curve), of the relative average effective field h (black dots) defined by

$$\overline{H}_{\text{eff}}=\int P(H)\,H\,dH, \tag{3}$$

and of the normalized values of the most probable field H_{eff} in the spectra (open circles). The dashed curve in Fig. 2 represents a graph of the function

$$B_S(\xi\sigma\tau^{-1}), \tag{4}$$

where B_S is the Brillouin function with the spin $S=1$; the parameter in the above equation is $\xi=1.6$; $\tau=T/T_C$ is the reduced temperature; the Curie temperature is $T_C=515$ K. It is clear from Fig. 2 that $\overline{H}_{\text{eff}}$ is proportional to the average magnetization throughout the investigated temperature range and that the behavior of the most probable field H_{eff} is best described by Eq. (4). The agreement between the temperature dependences of $\overline{H}_{\text{eff}}$ and the magnetization has been reported earlier for alloys of similar composition.[6,7] The expression (4) was first suggested in Ref. 8 and it was applied to the behavior of H_{eff} in the spectra of the Fe–Ni alloys in Ref. 9. According to Ref. 8, Eq. (4) describes the magnetization to a localized moment and the exchange interaction of this moment with the average magnetization is represented by the parameter ξ. If $\xi=1$, then Eq. (4) reduces to the ususal equation for the average magnetization in a system of localized moments considered in the molecular field approximation. An increase in ξ corresponds to enhancement of the exchange coupling between the moment and the magnetization. Therefore, the Fe atoms in Invar corresponding to the main maximum of $P(H_{\text{eff}})$ have a temperature-independent localized moment and the exchange interaction of this moment with the magnetization is stronger than the average in the alloy. Exactly as in the case of Fe–Ni alloys with higher nickel concentrations, we can assume that the magnetic moment is $\mu_{\text{Fe}}=2.8\mu_B$ (μ_B is the Bohr magneton). Fluctuations of the parameter ξ result in broadening of this maximum of $P(H_{\text{eff}})$ as temperature is increased. A detailed analysis of the influence of fluctuations of the exchange interactions on the form of $P(H_{\text{eff}})$ can be found in Ref. 5. We may assume that the volume of an Fe atom with a localized moment depends weakly on the temperature because the local polarization of the $3d$ energy band is retained at temperatures much higher than T_C (Ref. 10). This provides an additional confirmation of the hypothesis used above in the calculations that the Fe atoms corresponding to the main maximum of $P(H_{\text{eff}})$ make no contribution to the Invar anomaly. The Fe atoms responsible for a stronger compression of the lattice during heating of Invar correspond to $p(H_{\text{eff}})$ represented by Eq. (1) and their magnetic state is characterized by the value of H_{eff}, and the dependence of the atomic volume on H_{eff} is linear.

It is well known that H_{eff} of alloys has two main contributions. The first originates from the polarization of the ionic core and conduction electrons by the intrinsic magnetic

moment, whereas the second is due to the conduction electrons polarized by the moments of the neighboring atoms. As shown in Ref. 6, H_{eff} for Invar is governed only by the composition of the immediate environment. We then find that

$$H_{\text{eff}} = A\mu_{\text{Fe}} + B\mu. \quad (5)$$

Here, μ is the average moment per atom of the immediate environment; A and B are empirical constants. We can estimate A and B by assuming 90 and 50 kOe, found in Ref. 11 for Fe–Ni alloys of the non-Invar type.

In an ordered alloy in which the atomic environment of Fe is known exactly, the value of H_{eff} is related linearly to the atomic moment and the dependence of $(\Delta\nu/\nu)$ on this field is also linear. In the case of disordered Invar it is necessary to consider the influence of fluctuations in the immediate environment. An analysis of possible configurations, their statistical weight, and magnetization made using the experimental values $\bar{\mu}_{\text{Fe}} = 2.37\mu_B$ and $\bar{\mu}_{\text{Ni}} = 0.6\mu_B$ (Ref. 12) shows that these corrections are relatively small and that the linear dependence of $(\Delta\nu/\nu)$ is retained in the case of proportionality between μ_{Fe} and μ or the dependence becomes somewhat weaker. It should be stressed that this conclusion is not limited by any model representations and can be used to check the existing theories and model of the Invar anomaly.

The linear dependence of $(\Delta\nu/\nu)$ on the atomic moment does not agree with the recent results of theoretical energy band calculations or with the assumptions in the models used in Refs. 1, 3, and 13, according to which this dependence should be quadratic. However, the linear dependence of $(\Delta\nu/\nu)$ agrees well with Ref. 14, where it has been established for a series of iron alloys that the composition dependences of the lattice parameters are linear functions of the average magnetic moments. Another feature of this dependence $(\Delta\nu/\nu)$, which cannot be explained by the band models or the model of Ref. 2, are the negative values of $(\Delta\nu/\nu)$ in the range $H_{\text{eff}} \lesssim 60$ kOe. In fact, according to the band theory the polarization of local $3d$ energy band on transition of an alloy to the ferromagnetic state increases the kinetic energy of electrons which is proportional to the square of the moment. An increase in the kinetic energy is partly compensated by a reduction in the width of the local energy band because of an increase in the atomic volume. The thermal Schottky transition between states with different atomic volumes, which is the basis of the model of Ref. 2, also fails to predict negative values of $(\Delta\nu/\nu)$.

We shall assume that the linear relationship between the atomic volume and the moment is fundamental to the theory of Invar alloys. It may be explained by the polarization of some Fe atoms due to the exchange interaction with the localized moments in the immediate environment. Consequently, a magnetic moment appears at the Fe atoms and this is accompanied by a corresponding change in the volume. We can call this the "atomic magnetostriction" induced by the exchange magnetic field. It is interesting to note that, according to a theoretical expression for the magnetostriction induced by an external magnetic field[15] and a phenomenological analysis of this quantity,[10] the polarization of the Fe atoms increases the volume by an amount proportional to the resultant moment. The reduction in the atomic volume exhibited by some of the Fe atoms in the ferromagnetic state of Invar can be explained naturally by the appearance of moments antiparallel to the magnetization. This result is due to the dependence of the exchange fields inducing the moment on the interatomic distances. As first suggested in Ref. 16, the exchange integrals of the Fe–Fe atoms of pairs are negative, whereas those of the Fe–Ni pairs are positive. Therefore, if the net exchange field due to the immediate environment is positive, a moment parallel to the average magnetization appears at the central Fe atom. If the field is positive, then an antiparallel moment is induced. The improvement in respect of the energy in the parallel orientation is greater if the antiferromagnetic Fe–Fe interaction is additionally suppressed by an increase in the interatomic distance. It should be pointed out that, according to Refs. 3 and 17, the exchange integral decreases on increase in the lattice constant. In the antiparallel orientation the same considerations show that the interatomic distance and the atomic volume decrease. Since the Fe–Ni and Ni–Ni exchange integrals depend weakly on the distance,[17] we can say that in the parallel orientation of moments an Fe atom is repelled by Fe atoms from the immediate environment, whereas in the antiparallel orientation it is attracted to these atoms. Therefore in the case of Invar the polarization of the Fe atoms increases the atomic volume and, consequently, increases the interatomic distance irrespective of the sign of the exchange field. The repulsion between the Fe atoms with parallel moments also increases the interatomic distance. The attraction between atoms with antiparallel moments compensates the increase in the distance due to the polarization of the central Fe atom.

The Mössbauer data make it possible to support these qualitative considerations by quantitative estimates. The total intensity $p(H_{\text{eff}})$ near T_C corresponds to the immediate environment configurations with no more than three or four Ni atoms. Cooling reduces the intensity and at 4.2 K its value corresponds to Fe atoms with just one Ni atom in the environment. These Fe atoms have probably antiparallel moments since negative values of $(\Delta\nu/\nu)$ are deduced from the presence in the $P(H_{\text{eff}})$ structure of a maximum at low values of H_{eff}. In the case of other Fe atoms responsible for the Invar anomaly the polarization and H_{eff} increase a result of cooling and reach limiting values at 4.2 K. At this temperature we can assume approximately that the moment is $\bar{\mu}_{\text{Fe}} = 2.37\mu_B$, because at 4.2 K more than 90% of the Fe atoms correspond to the main maximum of $P(H_{\text{eff}})$. We used this estimate of the moment and replaced $(\Delta\nu/\nu)$ with the spherical atomic volume and we found that the latter depends linearly on μ_{Fe} at a rate of $2.3\%/\mu_B$. This is in good agreement with the value $2.25\%/\mu_B$ obtained in Ref. 14 from an analysis of the fcc lattice parameters of Fe and of Fe–Ni alloys with high Ni concentrations.

The results of the present paper enable us to propose a new model of the expansion anomaly of Invar, combining the features of the band and localized theories. It is shown that the Invar anomaly is due to the appearance of magnetic

moments at the Fe atoms which have no more than three or four Ni atoms in their immediate environment, and this effect is due to the exchange polarization by the nearest neighbors characterized by localized moments. The Fe atoms with no more than one Ni atom in the environment acquire a magnetic moment antiparallel to the average magnetization, whereas the other Fe atoms responsible for the Invar anomaly acquire a parallel moment. The polarization increases the atomic volume of iron and the action of the exchange field induces an attraction between the Fe atoms with the antiparallel moments and a repulsion between the Fe atoms with the parallel moments. As a result, the effective atomic volume depends linearly on the atomic moment.

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