3. A SURVEY OF THEORIES OF INVAR

3.1 Introduction

It may be that Invar behavior—the several remarkable characteristics of FCC Fe–Ni alloys in the Invar region of composition, particularly the drastic deviation of saturation magnetization from the Slater–Pauling curve and the disappearance of ferromagnetism associated with anomalies in various physical properties—gives a key for understanding the mechanism of ferromagnetism of iron-group transition metals. From this point of view, the Invar problem seems to be of great interest not only for metallurgists but also for physicists.

To discuss the Invar characteristics, the following points should be taken into consideration:

(1) The mechanism of disappearance of ferromagnetism.

(2) Thermal expansion, the Invar property in a narrow sense: that is, invariance of length due to very small thermal expansion seems to be very closely related to the drastic deviation of saturation magnetization from the Slater–Pauling curve. Very small, sometimes even negative, thermal expansion is observed in alloy systems which show drastic deviation from the Slater–Pauling curve, e.g., the FCC Fe–Ni, Fe–Pd and Fe–Pt systems. On the other hand, in alloy systems which have gradual deviation from the Slater–Pauling curve, e.g., the Fe–Mn and Ni–Mn systems, no Invar-like anomaly in thermal expansion is observed.

(3) Invar-like anomalies are observed in alloys with composition near the boundary of an $\alpha \rightleftharpoons \gamma$ transformation.

Theoretical explanations of the Invar phenomena are divided into two categories: one is crystallographic or metallurgical, connecting Invar properties with the existence of superstructure or with transformation of the crystal structure; the other is physical, connecting Invar properties with the mechanism of ferromagnetism of the alloy system.

Masumoto was the first to explain the Invar characteristics by connecting them with the mechanism of ferromagnetism. The guiding principle which he discovered in the investigation of Super Invar[1] and led him to the discovery of Stainless Invar[2] was a magnetic consideration: alloys with high magnetization and low Curie temperature may have small, even negative, thermal expansion. This is known as Masumoto's empirical rule.

Metallurgical theories before Masumoto's theory are surveyed in Sec. 3.2. Masumoto's theory is briefly reviewed in Sec. 3.3. Sec. 3.4 is devoted to Zarnetzki's and Dehlinger's theories, which are based on the volume dependence of the exchange interaction. Modern theories, which will be discussed in detail in Part IV, are surveyed in Sec. 3.5. In the concluding section, a short remark on the present stage of the theory of the Invar problem is given.

3.2 Theories before Masumoto's Theory

3.2.1 Discovery of Invar by Guillaume

Research on Invar alloys began with Guillaume in the last decade of the nineteenth century. As seen from the first paper[3] on Invar alloy by Guillaume, beginning with the phrase "Transformations magnétiques et dilatation," he was well aware that there was a relation between magnetic transformation and thermal expansion; he pointed out clearly that the temperature coefficient of thermal expansion is larger above the magnetic transformation temperature than below.

3.2.2 Systematic Investigation by Chevenard

In his systematic investigation on dilatation and specific volume of Fe–Ni alloys,[4] Chevenard proposed the existence of the compound Fe_2Ni and attempted to explain the Invar properties by relating them to the existence of this compound. To prove the existence of the compound, he referred to the fact observed by Weiss and Foëx, that the curve of saturation magnetization versus composition in the alloy system consists of two line segments meeting at the composition Fe_2Ni. He noticed that there is an analogy between anomalies in Fe–Ni and in water and suggested that polymerization of molecules, which had been able to explain most anomalies in water, could also give a sufficient explanation of Invar anomalies. As the temperature rises, one of the two polymerization states, $(Fe_2Ni)^\alpha$, stable at lower temperatures, partly transforms to the other state, $(Fe_2Ni)^\beta$, more dense, more rigid, and stable at higher temperatures; this contraction superposed on the normal thermal phenomena would result in the well-known anomalies of thermal expansion and elasticity of Invar. Chevenard also pointed out that the magnetostriction first observed by Nagaoka and

Honda* in Ni-steels could be explained by the appearance to some extent of the low temperature polymerization state as a result of isothermal magnetization of Fe–Ni alloys. This idea of two different polymerization states of the Fe_2Ni compound returned about fifty years later in a new form, as the idea of two electronic configurations of the γ-Fe atom, by Weiss.[5]

3.2.3 Contributions by Honda

(a) Lowering of the A_{r3} point of Fe by addition of Ni Honda and Takagi[6] pointed out that the curve of saturation magnetization versus composition in Fe–Ni alloys is smooth, rather than composed of two segments intersecting at the composition Fe_2Ni, and concluded from an examination of the equilibrium diagram of the Fe–Ni system that there is no evidence for the existence of the compound Fe_2Ni. They proposed another explanation, which takes no account of any compound, for the small thermal expansion of Invar. Noticing that the $A_3(\alpha \rightleftharpoons \gamma)$ transformation point of Fe is lowered by the addition of Ni, and that by cooling from higher temperature the expansion coefficient of irreversible Fe–Ni alloys decreases and then changes its sign in the vicinity of the A_{r3} transformation point (A_3 point on cooling), they claimed that the A_{r3} point of Fe is lowered by addition of Ni and that A_{r3} point of Invar lies near room temperature, resulting in the small thermal expansion. Answering the question why Invar does not have an irreversible transformation, they stated "35% Ni nickel steel is reversible down to the lowest temperature ever studied; but according to our view, it is an irreversible alloy, if we could cool it toward the absolute zero." From their experiments on the magnetic susceptibility of nickel steels as a function of temperature, which showed that the Curie law did not hold good except above 700°C, they pointed out that "the so-called Curie's constant for ferromagnetic substances is not really constant through a wide range of temperatures; only in a certain range of temperatures considerably above the critical point, does Curie's law hold good" and that "the Curie constant has therefore not an important meaning." Notwithstanding this claim, they tried to calculate the Curie constant for the range of temperature above 700°C. According to their result, there was no abrupt bend of the Curie constant versus composition curve at 35 wt.% Ni, in contrast with the result of Weiss and Foëx that the Curie constant of nickel steel plotted as a function of concentration consisted of two straight segments intersecting at 35 wt.% Ni, corresponding to the compound Fe_2Ni. Examining the results of Weiss and Foëx, they found the value of the Curie constant for pure iron had been taken 2.5 times too small; if the cor-

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* The data of Nagaoka and Honda on length and volume magnetostriction of the 36 wt.% Ni–Fe alloy are reproduced in the book *Ferromagnetism*, by R. M. Bozorth (D. Van Nostrand Co., Inc., New York, 1951) as Fig. 13–61 on p. 642.

rected value is taken, the curve bends rapidly upwards in approaching pure iron, as in the work of Honda and Takagi. They pointed out also that Weiss and Foëx had measured the susceptibility of only two compositions, 10 and 20 wt.% Ni, between pure iron and 30 wt.% Ni, so that the shape of the curve in question could not be precisely known; Honda and Takagi measured the susceptibility of six composition, with 2, 5, 8, 10, 15, and 23 wt.% Ni, between pure iron and 30 wt.% Ni steel.

Although the explanation connecting Invar characteristics with the A_3-transformation was later retracted by Honda himself, it is very interesting to observe the individuality of Honda, the positivist, in this criticism of Weiss and Foëx. It was characteristic of Honda, who was an experimental scientist concerned with the magnetism of metallic substances (which generally do not obey Weiss' law), that he could never accept Weiss' molecular field theory of ferromagnetism even to the end of his life.

(b) Invar behavior as a characteristic of γ-phase ferromagnetic alloys In a paper[7] devoted to precise determination by dilatometer of the beginning and ending points of the A_3-transformation during heating and cooling in the pure Fe–Ni system (not nickel steels), Honda and Miura pointed out that their investigation, and a work by Kase[8] on the equilibrium diagram of the Fe–C–Ni system, "show that at the concentration of Invar, the A_3-transformation has already been lowered to below -100°C, and hence does not take place in the vicinity of room temperature." Retracting the former theory by Honda and Takagi[6] relating the small thermal expansion of Invar to the A_3-transformation, Honda and Miura stressed that "In the case of invar, the range of temperature, in which the coefficient of expansion is very small, lies in the ferromagnetic region in the γ-phase, and hence this abnormal property can have no connection with the A_3-transformation. In fact this is a property characteristic of the ferromagnetic alloy in the γ-phase."

3.3 Masumoto's Theory—Ferromagnetic Expansion

It was Masumoto[1] who developed the above suggestion by Honda and Miura, connecting it with ferromagnetism of γ-phase Fe–Ni alloys. He was the first to attribute the Invar anomaly to the magnetic properties of the alloys. In considering the magnetism of the γ-phase Fe–Ni system, explanation of at least two phenomena is required: (1) the rather sharp drop of the saturation magnetization from the Slater–Pauling curve near 30 wt.% Ni and (2) the difference between composition with maximum saturation magnetization and that with maximum Curie temperature. Masumoto considered that the saturation magnet-

ization at 0 K naturally increases with Fe content while the Curie temperature has its maximum at the composition 35 wt.% Fe, as was observed; as a result of these two factors, the composition with maximum saturation magnetization at room temperature is displaced towards pure Fe compared with the composition with maximum Curie temperature. (The fact that even at very low temperature the saturation magnetization decreases rapidly near 30 wt.% Ni was found much later by Kondorsky and Sedov.[9])

According to Masumoto, the curves of thermal expansion vs. temperature in reversible Fe–Ni alloys, which contain more than 30 wt.% Ni, have a typical form shown schematically in Fig. 3.1. With increasing temperature, the expan-

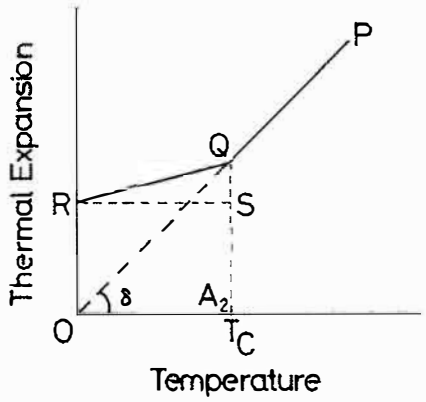

Fig. 3.1 Typical form of the curves of thermal expansion vs. temperature in reversible Fe–Ni alloys.

sion increases almost linearly up to the Curie point T_C, where the rate of change of expansion abruptly increases. Extending the straight line PQ of expansion above T_C down to room temperature O, we have OR, which represents the expansion caused by the ferromagnetic state of the alloy, i.e., the spontaneous magnetostriction. Masumoto called this quantity the "ferromagnetic expansion"; it can be obtained directly from thermal expansion data. Masumoto believed, from Honda's molecular theory of magnetism,[10] that the ferromagnetic expansion would be proportional to the saturation magnetization at room temperature for γ-phase solid solutions with varying concentration. He confirmed this experimentally by comparing the measured ferromagnetic expansion e_f with saturation magnetization at room temperature I_s for reversible Fe–Ni alloys of various compositions. Hence, putting $e_f = kI_s$ and denoting the inclination of the line OQ by the angle δ, which he took as nearly constant for all reversible alloys, he derived the thermal expansion coefficient α as

$$\alpha = \frac{QS}{RS} = \frac{QA_2 - SA_2}{\theta} = \tan\delta - \frac{kI_s}{\theta}, \tag{3.1}$$

where θ is the Curie temperature measured from room temperature. From this relation, he concluded that *alloys with high saturation magnetization and low Curie temperature could have very small, or even negative, thermal expansion.* This is Masumoto's empirical rule for Invar, which was found by him in the investigation of Super Invar[1] and led him to discovery of Stainless Invar.[2] This rule remains valid.

3.4 Theories Related to Volume Dependent Exchange Interaction

Kornetzki[11] and Dehlinger[12] attempted to explain Invar properties on the basis of the modern theory on magnetism.

Kornetzki[11] pointed out that it is possible to deduce the volume dependence of the exchange interaction from the change in volume of a ferromagnet when it is magnetized. According to the Weiss theory, magnetization $I(T, H)$ depends on the temperature, on the strength of the magnetic field, on the saturation magnetization at 0 K, I_0, and on the Weiss factor or the exchange interaction J. From the fact that the magnetization at constant temperature and constant field changes by application of pressure, i.e., by a change in volume, it is concluded that I_0 and/or J should depend on pressure or on volume. If I_0 is independent of volume (much later, Kondorsky and Sedov[9] showed this is not the case for Invar), J must depend on volume. This means the interaction between magnetic dipoles of atoms depends on the distance between them. Since the Curie temperature T_C is proportional to J, T_C also depends on volume. Kornetzki attributed the fact that the Fe–Ni alloy with 30 wt.% Ni, which is ferromagnetic at room temperature, entirely loses its spontaneous magnetization under a pressure of 10^4 atmosphere to the lowering of the Curie temperature below room temperature by application of the pressure.

Dehlinger[12] deduced the exchange integral J for each transition metal as a function of inter-atomic distance r from comparison of ferromagnetic saturation moments in various crystal lattices, and showed that the volume expansion due to magnetization (as in the case of Invar) is attributable to the behavior of J as function of r. Denote the atomic distance which makes J maximum by r_0, and the actual distance by d. For the case $d < r_0$, which Dehlinger considered to hold in all transition metals, the exchange force always trends to increase the atomic distance or the atomic volume when the metals are magnetic. Dehlinger expected that $J(d) < 0$ and $d < r_0$ for γ-Fe, $J(d) > 0$ and $d < r_0$ for Ni metal, and that the slope of J at d is steepest in γ-Fe. He attributed the small

expansion of Invar to a diminution of volume due to a change of state superposed on the normal thermal expansion. From the complete reversibility of the change in volume, he concluded that this change of state could not be accompanied by rearrangement of atoms, because any change of state due to rearrangement of atoms would be irreversible, and that the sole possible mechanism of the change of state must be magnetic. On the basis of this idea, and the behavior of J vs. r, he gave an explanation of the thermal expansion of Invar as follows: While the lattice binding force independent of magnetization tends to give an atomic distance smaller than r_0, the actual distance d is determined by a balance between the lattice binding force and the exchange force. The steeper is the slope of $J(r)$ at d, the larger is the expansion by magnetization. The slope of J at d is steepest for γ-Fe. If γ-Fe were ferromagnetic, the volume expansion due to magnetization in γ-Fe would be larger than that in other metals because of the steepness of J at d. But γ-Fe is not ferromagnetic, since $J(d) < 0$. Addition of some amount of Ni makes $J(d)$ positive. In the Invar alloy, which contains a sufficient amount of Ni, the value of $J(d)$ is positive while the steepness of the slope of J remains as in γ-Fe, resulting in a large volume contraction on the disappearance of magnetization.

We may say that the works of Masumoto, Kornetzki, and Dehlinger established an explanation of the expansion anomaly of Invar alloy that attributed it to a magnetic property, the spontaneous volume magnetostriction.

It should be noted that Mikura[13] pointed out that the contribution of conduction electrons to thermal expansion may be negative, provided the shape of the density-of-states near the Fermi level is appropriate. He suggested that the small expansion of Invar may be attributed to the cancellation of the normal positive expansion of the lattice by a negative contribution from the conduction electrons. Much later, Varley[14] proposed an idea similar to Mikura's on the possibility of a negative coefficient of thermal expansion.

3.5 Modern Theories

The peculiarity in the physical properties of Invar alloys, related intimately with magnetic effects, has made the Invar problem the subject of considerable attention by physicists, in addition to the interest of metallurgists in the investigation of these alloys because of their usefulness in technical applications. As the modern theories are developed in detail by various authors in Part IV, we give here briefly the essence of each theory and how it explains the characteristic phenomena summarized in Table 3.1. Also, we note whether or not the presence of Fe atoms is essential in each theory.

Table 3.1 Phenomena characteristic of the Invar alloy system.

(1)	Abrupt disappearance of spontaneous magnetization near the composition 30% Ni.
(2)	Discrepancy between the composition with maximum magnetization ($\sim Fe_{0.7}Ni_{0.3}$) and that with highest Curie temperature ($\sim Fe_{0.4}Ni_{0.6}$).
(3)	Large paraprocess (high field) susceptibility.
(4)	Small thermal expansion or large positive spontaneous volume magnetostriction.
(5)	Large positive forced volume magnetostriction or large negative pressure dependence of spontaneous magnetization.
(6)	Large negative pressure dependence of Curie temperature.
(7)	Presumed antiferromagnetism of Fe-rich FCC Fe–Ni alloys (above $Fe_{0.7}Ni_{0.3}$). These alloys cannot be prepared in the FCC structure.
(8)	Deviation of magnetization vs. temperature curve of Invar alloys from standard Brillouin functions.
(9)	Large residual electric resistivity.

3.5.1 Latent Antiferromagnetism

Taking the phenomenon (7) as the starting point of the argument, the theory based on latent antiferromagnetism explains the phenomena (1), (3), (5), and (9) and is expected to explain the phenomena (2), (8), and (6). The presence of Fe atoms plays an essential role.

Kondorsky[15,16] criticized the theories of Kornetzki[11] and Dehlinger[12] as they had not answered the question why the Invar peculiarities occur at 30–45% Ni. From the fact that 73% Fe–18% Cr–9% Ni alloy is antiferromagnetic below 40 K, he inferred the exchange integral J_1 between neighboring Fe atoms to be negative in the FCC structure. Using the exchange integrals J_1 defined above, J_{12} between neighboring Fe and Ni atoms and J_2 between neighboring Ni atoms, and assuming that the localized moment on each atom in the Fe–Ni alloy is equal to the mean moment per atom in the alloy, and that the ratio of the number of atoms with right spin to that with left spin in each constituent element of the alloy is equal to the ratio of the total number of atoms with right spin r to that with left spin l in the alloy, he deduced the total exchange energy U of an Fe–Ni alloy composed of N atoms as

$$U = -\frac{Nz}{2}\left(\frac{r-l}{r+l}\right)^2 (c_1^2 J_1 + 2c_1 c_2 J_{12} + c_2^2 J_2), \tag{3.2}$$

where z is the number of nearest neighbors and $c_1(=1-c_2)$ and c_2 are, respectively, the concentration of Fe and Ni. When the trinominal in the second parentheses of Eq. (3.2) is positive, the value of U is smallest for $l=0$, corresponding to a ferromagnetic state; when the trinominal is negative, the value of U is smallest for $l=r$ corresponding to an antiferromagnetic state. The

critical concentration of Ni, c_k, is given by

$$c_k = \frac{J_{12} - J_1 - (J_{12}^2 - J_1 J_2)^{1/2}}{2J_{12} - J_1 - J_2} \tag{3.3}$$

and the magnetization abruptly vanishes at $c_2 = c_k$ from its highest value. Provided

$$-J_1 \simeq J_{12} \simeq J_2, \tag{3.4}$$

Eq. (3.3) gives $c_k \simeq 0.3$, which explains satisfactorily the phenomenon (1).

It is possible to discuss the composition dependence of the Curie temperature by this model, although Kondorsky himself did not explicitly discuss it. Vonsovsky[17] had shown the Curie temperature T_C of a binary alloy with three kinds of exchange integrals between neiboring atoms to be given by

$$kT_C = z(c_1^2 J_1 + 2c_1 c_2 J_{12} + c_2^2 J_2) \tag{3.5}$$

for the case of complete disorder. The concentration of Ni, c_θ, of the alloy with the highest Curie temperature is derived from Eq. (3.5) as

$$c_\theta = (J_{12} - J_1)/(2J_{12} - J_1 - J_2). \tag{3.6}$$

Assuming condition (3.4) for J_1, J_{12} and J_2, we have for the T_C vs. composition curve a parabola, with its vertex at Ni ($c_\theta = 1$), crossing the abscissa at c_k. Although this value of $c_\theta (= 1)$ does not agree with observation ($c_\theta \simeq 0.6$), phenomenon (2), the discrepancy between c_k and c_θ, is qualitatively explained by this model. Another choice of values of the exchange parameters (larger J_{12} and smaller J_2) may give a more satisfactory result.

According to Kondorsky, there is a "latent" antiferromagnetic state between the ferromagnetic and antiferromagnetic states, in which some atoms have magnetic moments antiparallel to the total magnetic moment, as a result of local equilibrium. The latent antiferromagnetism occurs when the mean energy of Fe atoms with left spin, u_l, given by

$$u_l = z\left(\frac{r - l}{r + l}\right)(c_1 J_1 + c_2 J_{12}), \tag{3.7}$$

is negative, that is, when

$$c_2 < c_a = -J_1/(J_{12} - J_1). \tag{3.8}$$

For the case of $-J_1 \simeq J_{12}$, we have $c_a \simeq 0.5$, which fairly well explains the fact that the magnetization vs. composition curve of Fe–Ni alloy system starts to deviate from the Slater–Pauling curve near $Fe_{0.5}Ni_{0.5}$. Phenomena (3) and (9)

are explained by the existence of atoms with antiparallel spin due to the latent antiferromagnetism. Phenomenon (5) results from the change in c_k due to the change in J's by the application of pressure. Assuming relation (3.4), and $dJ_1/dp = dJ_{12}/dp = dJ_2/dp = dJ/dp$, we have

$$\frac{dc_k}{dp} = -\frac{1}{2\sqrt{2}J}\frac{dJ}{dp}, \tag{3.9}$$

which gives $dc_k/dp > 0$ provided $dJ/dp < 0$. This means that by application of pressure c_k shifts to the Ni-rich side and the magnetization decreases. It is easily seen from Eq. (3.5) that a negative dJ/dp gives negative pressure dependence of Curie temperature, phenomenon (6). It should be noted that as pointed out by Terao and Katsuki[18] and later by Colling and Carr,[19] the spontaneous volume magnetostriction should be distinguished from the forced volume magnetostriction and the latent antiferromagnetism model does not, by itself, explain phenomenon (4), the thermal expansion anomaly.

Kondorsky and Sedov[9,16] found that for Fe–Ni alloys in the Invar composition region the magnetization is considerably smaller even at 0 K than that given by the Slater–Pauling curve, and that the change in magnetization due to pressure does not vanish even at 0 K, contrary to Kornetzki's expectation.[11]

Proposing a noncollinear alignment of atomic magnetic moments, Sidorov and Doroshenko[20,21,22] gave an expression for the composition dependence of magnetization of a binary alloy system with negative J_1 and positive J_{12} and J_2, in terms of parameters μ_1 and μ_2, the atomic moments of the first and second elements respectively, and c_k, the critical concentration of the second element at which the contribution to the net magnetization from each component vanishes. Using values of c_k determined by experiments and reasonable values of atomic moments ($\mu_{Ni} = 0.6\mu_B$, $\mu_{Fe} = 2.8\mu_B$, $\mu_{Mn} = 3.2$ or $3.6\mu_B$ and $\mu_{Pd} = 0.35\mu_B$), they obtained good agreement with observations for FCC Fe–Ni,[21,22] FCC Mn–Ni[20,22] and FCC Fe–Pd[22] alloys. Although they have not answered the question why c_k is about 0.3 in the Fe–Ni alloy system (they have taken $c_k = 0.3$ as a given parameter), they have shown that the latent antiferromagnetism model with noncollinear alignment of atomic moments can relate consistently the composition dependence of magnetization to the critical composition. Dubinin, Sidorov, and Valiev[23] calculated the composition dependence of the Curie temperature and the temperature dependence of magnetization on the basis of this model. They obtained a result in good agreement with experiments; phenomena (2) and (8) were explained.

Odagaki and Yamamoto[24] discussed the composition dependence of magnetization of binary alloys with negative J_1 and positive J_{12} and J_2, using a computer simulation method.

3.5.2 Two Electronic Configurations of the γ-Fe Atom

Taking phenomena (1) and (7) as a starting point, the theory based on the idea of existence of two electronic configurations in the γ-Fe atom explains phenomena (2), (4), (6), and (8). Fe atoms play an essential role.

Weiss[5] attempted to explain the Invar anomalies by applying to the FCC Fe–Ni system the idea that a γ-Fe atom has two electronic states, one of which is an antiferromagnetic γ_1-state with low volume and low spin value and the other a ferromagnetic γ_2-state with high volume and high spin value. He suggested that the transition between γ_1- and γ_2-states does not occur as a first order transition but rather as an internal electronic excitation. He assumed that the energy difference between the two electronic states of a γ-Fe atom in FCC Fe–Ni alloys depends on the Ni content, and that the γ_2-state is stable in alloys with more than 29 at.% Ni, while the γ_1-state is stable in pure γ-Fe. These assumptions are based on phenomena (7) and (1). In the alloys where the γ_2-state is stable, a decrease of volume due to thermal excitation of the γ_1-state with increasing temperature acts in opposition to the normal expansion of the lattice and gives a very small resultant expansion coefficient. We may regard the Weiss theory to be in some sense a revival of Chevenard's theory[4] by reading "the two polymerization states of the compound Fe_2Ni" in the latter as "two electronic states of the γ-Fe atom." From the fact that the lattice parameter vs. temperature curves show no abrupt anomaly, but rather a smooth variation through the Curie temperature, Weiss inferred that the anomaly in thermal expansion has little to do with effects at the Curie temperature or any magnetic effects, e.g., spontaneous volume magnetostriction. Assuming an appropriate dependence of the energy difference ΔE between the γ_1- and γ_2-states on the Ni content c in the FCC Fe–Ni system, he calculated the Curie temperature, magnetization at 0 K, magnetization as a function of temperature, and the shift of the Curie temperature with pressure for each alloy, as well as the lattice constant as a function of temperature. He has not answered the question why c_k is about 0.3, but has taken it as a premise in his discussion by choosing a ΔE-c curve to give an abrupt drop of magnetization at 29 at.% Ni. For the calculation of the Curie temperature T_C, he used an empirical expression of his own:

$$T_C \simeq 113.5\,|z\uparrow - z\downarrow|\,\ln(2S + 1), \tag{3.10}$$

where S is the spin quantum number of the atom, and $z\uparrow$ and $z\downarrow$ are the number of nearest neighbors of a particular atom with spin direction favored and opposed by the sign of the exchange integral. Evaluating the mean value of $2S$ and $|z\uparrow - z\downarrow|$ at T_C from the assumed ΔE–c curve, he calculated T_C from Eq. (3.10) and obtained a composition dependence of T_C in agreement with observation. According to Weiss, phenomenon (2), the difference between compositions

with the highest Curie temperature and with the largest magnetization, is attributed to the fact that there is thermal excitation of the γ_1-state at T_C, but not at 0 K. Phenomena (8), the deviation of the magnetization vs. temperature curve from the standard Brillouin functions, and (6), the decrease in Curie temperature with pressure, are also attributed to the effect of thermal or pressure excitation of the γ_1-state.

There are some other explanations of the Invar anomalies which somewhat resemble the Weiss theory.

To explain the magnetic properties of FCC Fe–Ni–Mn ternary alloys, Shiga[25] proposed the idea that the local moment at Fe sites is "induced" in antiferromagnetic alloys and "permanent" in ferromagnetic alloys, and that in Invar alloys a substantial local moment is induced at Fe site below the Curie temperature in addition to the permanent moment. Examining the cohesive energy due to band electrons, Shiga and Nakamura[26] pointed out that an induced magnetic moment should be accompanied by a volume expansion. Their idea resembles Weiss' in postulating more than one state for the Fe atom in the FCC lattice; according to them, however, the thermal expansion anomaly is connected to the magnetic properties, in contrast to Weiss model; the antiferromagnetic expansion in Fe–Ni–Mn alloys, which contradicts the Weiss model, is explainable within the framework of their model. Later, Shiga[27] noticed that there is a close resemblance between the deviation of the lattice constant from Vegard's law and the deviation of the magnetization in the FCC Fe–Ni alloy system from the Slater–Pauling curve, and proposed a simple equation for the lattice constant $a(x)$ of an alloy with composition $A_{1-x}B_x$:

$$a(x) = a_0^{A}(1 - x) + a_0^{B}x + C\mu(x), \tag{3.11}$$

where $\mu(x)$ is the average atomic moment of the alloy and a_0^{A}, a_0^{B} and C are adjustable parameters. For FCC Fe–Ni alloys, he calculated $a(x)$ vs. x, using observed values of $\mu(x)$ and adjusted values of the parameters and found excellent agreement between the calculated $a(x)$ values and the lattice constants at 0 K (estimated from thermal expansion measurements). Examining the lattice constant vs. composition curve at various temperatures, he concluded that in the Ni-rich region the magnetic term does not disappear above T_C, which means that localized moments persist above T_C; in the Fe-rich region, particularly in the Invar region, the magnetic term decreases with increasing temperature, which implies the collapse of the localized moments at high temperatures. The decrease of the magnetic term is responsible for the anomalous thermal expansion of Invar alloy. Shiga considered that Weiss' γ_2- and γ_1- states of the Fe atom correspond to the states with localized and delocalized magnetic moment.

Schlosser[28] proposed that FCC Fe–Ni alloys occur in three regions: the

region of the compound $FeNi_3$ with perfect order, the region of FCC Fe, and an intermediate region. The electronic configuration of an Fe atom is determined by the local atomic environment, or the number of neighboring Ni atoms. Based on this assumption, he attributed the anomalous properties of Invar to the amount of the intermediate region in the alloy.

3.5.3 Spin Wave Instability

A qualitative explanation of phenomena (1), (2), (5), and (7) is given by a consideration of spin wave instability of ferromagnetism in the band model. Fe atoms play no essential role.

Katsuki[29] considered that a theory of Invar characteristics based on the band model without highly artificial assumptions is preferable, because the spontaneous magnetization of the FCC Fe–Ni alloy system lies fairly well on the Slater–Pauling curve except the Invar region, and the temperature coefficient of the electronic specific heat is large for these alloys. While Kondorsky's theory[15,16] had been based on a localized electron model and Weiss' theory[5] had been based on the artificial assumption of a ΔE–c relation for two electronic states of the Fe atom in FCC Fe–Ni alloys, Katsuki proposed another interpretation based on the band model. Provided the number of 4s-electrons is 0.6 per atom, the number of 3d-electrons is just eight per atom for $Fe_{0.7}Ni_{0.3}$, and the upper sub-band is just half-filled if the 3d-band is composed of two sub-bands, an upper one accommodating four electrons and a lower one holding six electrons per atom. If the strongly ferromagnetic state were the ground state, then the exchange stiffness D (the coefficient in the spin-wave dispersion relation, $\hbar\omega_q = Dq^2$) would be negative and the strongly ferromagnetic state would become unstable, resulting in the vanishing of magnetization. This is the reason why the magnetization abruptly vanishes near $Fe_{0.7}Ni_{0.3}$ [phenomenon (1)]. From a consideration of a calculation of D by Katsuki and Wohlfarth[30] for a system of tightly bound s-electrons in a simple cubic lattice, Katsuki inferred that in a ferromagnetic alloy system the following relation will hold:

$$n(\text{ferro:start}) < n(D\text{:max}) < n(T_C\text{:max}) < n(M\text{:max}), \qquad (3.12)$$

where n is the number of electrons (or holes) per atom, and the phrases in parentheses mean the onset of ferromagnetism, the maximum value of D, the maximum of T_C, and the maximum in magnetization M (or the abrupt disappearance of M). Relation (3.12) includes phenomenon (2). For FCC Ni–Cu and Fe–Ni alloys, the value of the number of holes corresponding to each term of (3.12) is, in turn, 0 ($Cu_{0.6}Ni_{0.4}$), 0.6 (Ni), 1.4($Fe_{0.4}Ni_{0.6}$) and 2.0 ($Fe_{0.7}Ni_{0.3}$) per atom, provided the number of 4s–electrons is 0.6 per atom. For alloys with negative D, the ferromagnetic state, which is stable with respect to the paramag-

netic state, is unstable to the spin wave excitations, and it is expected that an antiferromagnetic state (in a broad sense) will appear. This explains qualitatively phenomenon (7). The spin wave instability model is not incompatible with the theory of spontaneous volume magnetostriction at 0 K for metallic ferromagnets proposed later by Katsuki and Terao.[31] They showed also that[32] the pressure coefficient of D is negative for the alloys with small D and that the critical composition at which D just vanishes in FCC Fe–Ni system shifts towards the Ni-rich side by application of pressure, resulting in a negative pressure dependence of the magnetization [phenomenon (5)].

3.5.4 A Theory Based on a Band Calculation

Starting from a calculated band structure of Ni,[33] Yamashita, Namba and Asano[34] made a test for the instability of the paramagnetic state with respect to the ferromagnetic and antiferromagnetic states with infinitestimal magnetic moment induced on each atom in FCC 3d-transition metals and alloys. The paramagnetic state was found to be unstable with respect to the ferromagnetic state for $n > 7.8$, and with respect to the ferromagnetic and antiferromagnetic states for $n < 7.8$, where n is the number of 3d electrons per atom. It is expected that the ferromagnetic state exists above $n = 7.8$, and a more complex magnetic structure, antiferromagnetic in a broad sense, may appear below $n = 7.8$. This work suggests that a serious band calculation can give a satisfactory explanation of phenomena (1) and (7).

3.5.5 Ferromagnetism Not Satisfying the Stoner Condition

A theory based on ferromagnetism not satisfying the Stoner condition gives an explanation of Phenomena (1), (2), (3), (4), (5), (6), and (7). Fe atoms play no essential role.

Assuming FCC Fe–Ni alloys to have the density-of-states curve calculated for FCC Ni metal by Wakoh and Yamashita[33] and to have a common value of exchange parameter adjusted to give a spontaneous magnetization of 0.6 μ_B/atom for Ni metal, Mizoguchi[35] showed that the critical composition at which the spontaneous magnetization suddenly vanishes is $Fe_{0.71}Ni_{0.29}$, i.e., $e/a = 8.58$, where e/a is the number of 3d + 4s electrons per atom. The Stoner condition with the adjusted value of the exchange parameter is not satisfied for $e/a < 9.1$, i.e., for alloys with more than 45 at.% Fe. Mizoguchi calculated also the energy difference ΔE between the ferromagnetic state and the paramagnetic state by making use of the value of the exchange parameter, and showed that the minimum of ΔE (the maximum of $|\Delta E|$) appears at $Fe_{0.3}Ni_{0.7}$, which is near the maximum Curie temperature. He explained phenomena (1) and (2).

Shimizu and Hirooka[36] calculated ΔE, T_C and the paraprocess (high field) susceptibility for each composition of FCC Fe–Ni, using a density-of-states

curve constructed from low temperature specific heat data for FCC Fe–Ni and Ni–Cu alloys based on the rigid band model. In their calculation, the value of the exchange parameter was adjusted for each alloy to give the observed value of spontaneous magnetization of the alloy. They showed that strong ferromagnetism appears for $e/a > 8.34$, while the Stoner condition is not satisfied for $e/a < 8.89$, and that the calculated Curie temperature has its maximum at $e/a \simeq 9.0$. They also calculated[37] the paraprocess susceptibility and the temperature dependence of magnetization at 0 K of each alloy, assuming the fluctuation of local composition given by Kachi, Asano and Nakanishi.[38] They showed that the susceptibility is mainly due to the shift of the critical composition towards the Fe-rich side by the application of a magnetic field, and that dM/dT does not vanish even at 0 K for Invar alloys. They explained phenomena (1), (2), (3), and (7). Later Shimizu[39] proposed a metastable mixing of ferromagnetic and paramagnetic phases in Invar alloy.

Criticizing the rigid band approximation as fallacious, Hasegawa and Kanamori[40] applied the coherent potential approximation to atomically disordered ferromagnetic binary alloy systems, especially to the FCC Fe–Ni system. Examining the deformation and the relative shift of density-of-states curves with up-spin and with down-spin, they obtained for alloys of various composition the average magnetic moment on Fe sites and on Ni sites, and the total magnetic moment of the alloy. It was shown that the total magnetic moment begins to deviate from the Slater–Pauling curve at about 50 at.% Fe, in agreement with experiments. The calculated T_C is too high, and the shape of the T_C vs. composition curve is dissimilar to the observed one.

Taking as parameters the ratio of the exchange parameter J to the band width W and the ratio J'/W', where J' and W' are the volume derivatives of J and W, Katsuki and Terao[18,31] formulated the magnetovolume effects of the itinerant electron ferromagnet at 0 K in the framework of the Stoner model. They applied it to a system with a step-type density-of-states curve, which is the simplest model showing the most essential character of the 3d-band of FCC transition metals. They calculated the spontaneous volume magnetostriction ω_s at 0 K with various electron (or hole) concentrations.[31] The calculated ω_s vs. concentration curve is in good agreement with the curve estimated from the observed thermal expansion anomaly in the FCC Fe–Ni alloy system. They explained why the spontaneous volume magnetostriction of Invar is large and positive in vivid contrast to that of Ni which is small and negative. Examining the volume dependence of J/W, they showed also that the critical composition shifts towards the Ni-rich side by application of pressure, resulting in a negative pressure dependence of the magnetization of Invar alloy.[41] They extended their theory to non-zero temperatures and calculated the magnetic contribution to thermal expansion and the pressure dependence of the Curie temperature.[42] A

qualitative agreement of the calculated magnetic contribution to thermal expansion with the observed anomalous part of the thermal expansion was obtained. Composition dependence of calculated relative Curie temperature and of the pressure derivative of relative T_C are in agreement with experiments, although the calculated values of T_C itself are too high. Phenomena (4), (5), and (6) are explained.

3.5.6 Very Weak Itinerant Electron Ferromagnetism

Mathon and Wohlfarth[43] noted that the observed Curie temperature of FCC Fe–Ni alloys between 25 and 50 at.% Ni varies with Ni content c as $T_C^2 \sim (c - c_0)$, where c_0 is 25 at.%,[44,45] and that this relationship follows from the theory of very weak itinerant electron ferromagnetism.[46,47] They claimed[43] that the Invar alloys are very weak itinerant electron ferromagnets, and that phenomena (3), (4), (5), (6), and (8) plus the fact that the composition dependence of the spontaneous magnetization is determined mainly by the electron concentration[48] are explainable by this model. They regarded phenomenon (1) to be the result of a *gradual* (not *abrupt*) transition from strong to very weak itinerant electron ferromagnetism arising from the existence of a minimum in the density-of-states curve near the concentration c_0.[49] Expanding the theory based on this model to a discussion of magnetovolume effect,[50] Wohlfarth[51,52] compared Invar alloys with $ZrZn_2$ (a typical material with very weak itinerant electron ferromagnetism) in magnetic properties, especially in pressure dependence of Curie temperature and the thermal expansion coefficient. He concluded that *$ZrZn_2$ is an Invar-type material* but with an effective degeneracy temperature down by about an order of magnitude from the values of the usual FCC Fe alloys. Of course, Fe atoms do not play any essential role in this model; even $ZrZn_2$ is regarded as an Invar-type material. In fact, a decrease of the Curie temperature by application of pressure[53] and a negative magnetic contribution to the thermal expansion[54,55] are observed in $ZrZn_2$. It may be commented here that the necessary condition for very weak itinerant electron ferromagnetism,[47]

$$\left[\frac{\nu'(\varepsilon_F)}{\nu(\varepsilon_F)}\right]^2 - \frac{1}{3}\left[\frac{\nu''(\varepsilon_F)}{\nu(\varepsilon_F)}\right] > 0, \tag{3.13}$$

where $\nu(\varepsilon)$ is the density of states, $\nu'(\varepsilon_F) = d\nu/d\varepsilon$ at $\varepsilon = \varepsilon_F$ and $\nu''(\varepsilon_F) = d^2\nu/d\varepsilon^2$ at $\varepsilon = \varepsilon_F$, is not satisfied for alloys with a minimum in the density-of-states curve at the Fermi level. Mathon and Wohlfarth[56] also derived an expression for the pressure dependence of the exchange stiffness D and showed that there is a close relation between dD/dp and dT_C/dp in a very weak itinerant electron ferromagnet; both derivatives are large and negative. Thus they explained the experimental result of Gustafson and Phillips[57] on the pressure dependence of

D in FCC Fe–Ni alloys.

Shiga[58] discussed the pressure dependence of the Curie temperature based on the itinerant electron model. He assumed that the intra-atomic Coulomb interaction U and a numerical factor G, which appear in an expression[59] for the effective exchange interaction J,

$$J = \frac{U}{1 + GU/W}, \tag{3.14}$$

are independent of the band width W; he calculated the unenhanced Pauli susceptibility χ_0 by expanding the formula for χ_0 in powers of $(kT)^2$ and neglecting higher order terms. He obtained the Curie temperature as a function of W from the relation $J\chi_0(T_C) = 1$. Assuming the band width W to vary with atomic spacing d as $W \propto d^{-5}$, he calculated the pressure dependence of the Curie temperature and obtained a negative dT_C/dp.

3.5.7 Local Fluctuation in Magnetic Properties

Tino and his colleagues[60-62] examined experimentally the temperature dependence of Young's modulus,[60] of the paraprocess susceptibility,[60] of the forced volume magnetostriction,[61] the Mössbauer effect[61] and the effect of thermal cycles on the thermal dilatation[62] for annealed and cold-worked Fe–Ni alloys in the Invar region, and concluded that the Invar alloy is a heterogeneous assemblage consisting of various small regions with different Curie temperatures. The heterogeneity is attributable to embryos of the α-phase dispersed in the γ-phase matrix. They claimed that the facts that alloys with Invar characteristics always lie near the boundary between α- and γ-phases in Fe–Ni, Fe–Pd and Fe–Pt systems and that the physical properties of Invar are affected considerably by cold work are understandable on this model. According to them, such heterogeneity is essential to the Invar characteristics.

By means of the Mössbauer effect, Nakamura, Shiga, and Shikazono[63] measured the internal field in FCC Fe–Ni alloys between 30 and 34 at.% Ni (later, Asano[64] between 20 and 30 at.% Ni) by using finely powdered samples in which the $\gamma \rightarrow \alpha$ martensitic transformation could be suppressed. They found that paramagnetic regions coexist with normal ferromagnetic regions in the alloys less than 32 at.% Ni even at liquid nitrogen temperature, which is much lower than the Curie temperature. They supposed that the paramagnetic regions originate from antiferromagnetic regions with the Néel point well below liquid nitrogen temperature and that the ferromagnetic and antiferromagnetic regions arise from statistical composition fluctuations in the alloy. The coexistence of ferromagnetic and antiferromagnetic regions is also deduced by Nakamura and Miyata[65] from an experimental investigation of exchange anisotropy in the FCC Fe–Ni–Mn ternary alloy system.

To explain the saturation magnetization of FCC Fe–Ni alloys between 20 and 30 at.% Ni measured by themselves on finely powdered samples, Kachi, Asano and Nakanishi[38] proposed that the fluctuation of the local composition in the alloys obeys a Gaussian distribution,

$$f(x, c) = \pi^{-1/2} h \exp\left[-h^2(x - c)^2\right], \tag{3.15}$$

where c is the mean atomic concentration of Ni and x is the local atomic concentration of Ni; the value of h was taken as 12. Using this distribution function, they explained the composition dependence of the lattice constant in the FCC Fe–Ni system,[66] obtained the temperature dependence of the thermal expansion coefficient for each alloy[67] and inferred the Curie temperature of the ideally uniform alloy[68] from the Curie temperature observed by Crangle and Hallam[45] and by themselves.[68] The distribution function (3.15) was also used by Shimizu and Hirooka[37] to calculate the paraprocess spin susceptibility and the temperature derivative of magnetization, and by Terao and Katsuki[41] to calculate the pressure dependence of the magnetization.

3.5.8 An Idea Based on Zener's Model of Ferromagnetism

Colling and Carr[19] recalled Zener's model of ferromagnetism,[69] which assumes that there exist two competing exchange interactions in metals, one of which is a ferromagnetic coupling of localized atomic spins via conduction electrons and the other is a direct antiferromagnetic coupling of localized atomic spins due to overlap of neighboring wave functions. The former coupling depends weakly on strain, while the latter depends strongly on strain. Colling and Carr proposed an explanation of phenomena (4) and (7) as follows. For a given atomic spacing the direct coupling of Fe atoms is larger than that of Ni atoms, and in FCC Fe–Ni alloys the overlap of Ni atoms is assumed to be negligible, whereas that of Fe is large enough to produce antiferromagnetism at a sufficiently high concentration of Fe. Parallel spins on neighboring Fe atoms are unfavorable with respect to the highly spin-dependent direct coupling, and they repel one another. Antiparallel spins will attract. Thus ferromagnetic Fe expands the lattice at low temperature and a contraction is produced with increasing temperature, resulting in a small net thermal expansion.

3.6 Conclusion

We have given a short survey of theories of Invar. In brief we may say that we have not yet any conclusive theory of the Invar problem. The principal difficulties seem to arise from the fact that Invar is an *alloy* and that materials with Invar characteristics always lie near the boundary between α- and γ-phases. Of the

present phase of the theory, we may say that it is in a stage where some simple interpretations based on different philosophies have been tentatively proposed. About fifty-five years ago, Guillaume[70] stated in his lecture on the anomaly of the nickel-steels that "There is as yet no complete and final theory of the phenomena exhibited by the nickel-steels; it is, however, possible to present a tentative sketch throwing light on the main causes of these phenomena." This statement seems to be still valid.

It is hoped that by publication of this book, readers will be freshly stimulated and led to an ambitious intellectual venture on the Invar problem.

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