Phenomenological theory of magnetoelastic interactions in Invars and Elinvars

É. Z. Valiev

Institute of Metal Physics, Ural Division, Academy of Sciences of the USSR, Sverdlovsk
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Ferromagnetic Invar and Elinvar alloys are considered as ferromagnets with strong magnetoelastic interactions. A systematic treatment of the phenomenological theory of magnetoelastic interactions in Invars and Elinvars is given. The thermodynamic quantities (thermal expansion, elastic constants, magnetic properties) and dynamical properties (propagation of acoustic waves and spin waves) are calculated theoretically. The combined effect of magnetization fluctuations and volume deformations is considered, as well as the effect of fluctuations on the thermodynamic properties. The theoretical results are compared to experiment and it is shown that the phenomenological theory gives a satisfactory quantitative explanation of the anomalies in the properties of Invars and Elinvars. The cause of the strong magnetoelastic interaction in Invars is discussed.

1. INTRODUCTION

The Invar problem has a history going back more than 50 years. The term "Invar" comes from the Latin *invariabilis*, meaning unchanged and refers to the constant length of an iron-nickel alloy bar near room temperature. This property was first observed by S. Hill in 1899. For this discovery he received the Nobel prize in 1920.

A detailed discussion of the history of the problem is given in Refs. 1–4. These books contain extensive information on the anomalous thermal, elastic, and magnetic properties of Invars (materials possessing Invar or Invar-like properties). The composition, properties, and region of engineering application of Invar alloys are described. Dozens of different models explaining Invar properties are discussed. These books, particularly Ref. 3, contain an extensive bibliography of references up to 1986.

Experiment shows that in ferromagnetic Invar alloys such as $Fe_{65}Ni_{35}$, $Fe_{72}Pt_{28}$, and others, there are large magnetovolume effects, together with anomalies in the coefficient of thermal expansion and in the elastic properties. In particular, the dependence of the Curie temperature T_c on pressure ($\partial T_c/\partial P$), the dependence of the magnetization on pressure ($\partial M/\partial P$), and the induced volume magnetostriction $\partial\omega/\partial H$ are all large. These facts suggest strong coupling between the magnetic and elastic properties in Invar alloys. Further progress in the solution of the problem is held back by the lack of a reliable theory, which would make it possible to calculate Invar effects.

Ferromagnetic or antiferromagnetic Elinvars (elastic Invars) are similar in composition and properties to Invar alloys. Elinvars are characterized by a constant value of the Young's modulus E in a certain temperature interval.[1–4] It is evident that Invar and Elinvar effects are both caused by the magnetoelastic interaction.

In the present review article we describe the phenomenological theory of magnetovolume interactions (MVI) and the application of this approach to obtain quantitative estimates of the anomalous properties of Invar and Elinvar alloys. The magnetovolume interaction is that part of the magnetoelastic interaction which depends only on pure volume deformations (to first order in the deformations) and only on the magnitude of the magnetization **M**. The magnetovolume interaction depends only on M^2 because it results from a change in the exchange energy of the material in the presence of deformation. Our review is based on results extending the ideas put forth in the works of Belov,[4] Wohlfart,[5] Shimizu,[6] and others.

Here we will atempt to show: 1) the effect of magnetovolume interactions on the thermodynamic and dynamical properties of ferromagnets in the most complete form possible; 2) that Invars and Elinvars are ferromagnets with strong magnetovolume interactions and their properties can be explained in terms of the phenomenological theory. A large number of calculated MVI effects agree with experiment to within a few dozen percent for Invars and Elinvars.

The problem of magnetovolume interactions is also of purely theoretical interest and represents one of the basic problems of the physics of magnetism in compounds of 3d-elements at finite temperatures.

In the theory of interacting subsystems (magnetic and lattice) the interaction is expressed as a change (renormalization) of the ground state (volume, magnetization) and of the excited states (phonons, magnons). In this approach the contributions from the renormalizations of the ground and excited states to the thermodynamic properties of the combined system can be separated. From this point of view, the publications on the magnetovolume interaction in ferromagnets can be divided into three groups. The first group considers the consequences of the renormalization of the ground state (spontaneous volume magnetostriction).[4–6,7–9] Magnetic fluctuations were taken into account in Refs. 7–9. Most of the papers in this group assume a model of a ferromagnet with collective electrons.

The second group[10,11] is based on the Heisenberg model. The change in the excited states and their effect on the thermodynamic properties are considered, while the renormalization of the ground state is not taken into account.

The third group takes into account the effect of renormalized phonons on the magnetic properties of ferromagnets with collective electrons.[12,13] We note that Refs. 12 and 13 actually are not included in the theory of interacting subsystems. The changes in the phonon frequencies induced by magnetovolume interactions are considered first, and then the effect of this change on the magnetic properties is considered. In the theory of interacting subsystems, on the other

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hand, magnetovolume interactions affect the phonon and magnetic properties simultaneously. We note that these three groups of papers are being developed practically independently of one another.

Hence there is a need for a systematic treatment of the theory of magnetovolume interactions capable of comparing the different approaches used in this theory. The phenomenological theory is useful in determining which magnetovolume effects must be considered in the phenomenological approach and which can be left for analysis in the microscopic theory. It will be convenient to postpone the answer to this question until the final section, however.

Kinetic properties of Invars and the effect of magnetovolume interaction on the kinetic properties of ferromagnets are outside the scope of this review article. The bibliography given here is illustrative, but not exhaustive.

2. DERIVATION OF THE THERMODYNAMIC RELATIONS FROM THE EQUATIONS OF STATE IN DIFFERENTIAL FORM

We consider the relations between the thermodynamic quantities characterizing the magnetic and nonmagnetic properties of the ferromagnet, as determined from the differential equations of state. The independent variables are chosen to be the temperature T, pressure P, and magnetic field H. The volume V, magnetization M, and entropy S are functions of T, P, and H. The ferromagnet is assumed to be infinite and with a single domain.

The equations of state in differential form are

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,H} dT + \left(\frac{\partial V}{\partial P}\right)_{T,H} dP + \left(\frac{\partial V}{\partial H}\right)_{T,P} dH, \quad (2.1)$$

$$dM = \left(\frac{\partial M}{\partial T}\right)_{P,H} dT + \left(\frac{\partial M}{\partial P}\right)_{T,H} dP + \left(\frac{\partial M}{\partial H}\right)_{T,P} dH, \quad (2.2)$$

$$dS = \left(\frac{\partial S}{\partial T}\right)_{P,H} dT + \left(\frac{\partial S}{\partial P}\right)_{T,H} dP + \left(\frac{\partial S}{\partial H}\right)_{T,P} dH. \quad (2.3)$$

The derivation of the thermodynamic relations for the jumps in the coefficient of volume expansion and the bulk modulus at the Curie point is somewhat different (see Ref. 4a, Ch. IV).

We will concentrate on the magnetic and elastic properties of the ferromagnet, although if necessary (2.1)–(2.3) can be used to obtain relations between the thermal quantities (heat capacity, magnetocaloric effect, and so on).

The differential relations (2.1) and (2.2) are coupled equations of state for the magnetic and elastic subsystems. The coupling constants are $\partial V/\partial H$ and $\partial M/\partial P$, which obey the well-known relation

$$\frac{\partial M}{\partial P} = -\frac{1}{V}\frac{\partial V}{\partial H}. \quad (2.4)$$

We obtain from (2.1) with $M = \text{const}$ and $T = \text{const}$

$$\left(\frac{\partial V}{\partial P}\right)_{M,T} = \left(\frac{\partial V}{\partial P}\right)_{H,T} + \left(\frac{\partial V}{\partial H}\right)_{P,T}\left(\frac{\partial H}{\partial P}\right)_{M,T}, \quad (2.5)$$

and from (2.2)

$$\left(\frac{\partial M}{\partial P}\right)_{T,H} = -\left(\frac{\partial M}{\partial H}\right)_{T,P}\left(\frac{\partial H}{\partial P}\right)_{M,T}. \quad (2.6)$$

Using (2.5), (2.6), and (2.4)

$$\left(\frac{\partial V}{\partial P}\right)_{M,T} = \left(\frac{\partial V}{\partial P}\right)_{H,T} + \frac{1}{V}\left(\frac{\partial V}{\partial H}\right)^2_{T,P}\left(\frac{\partial M}{\partial H}\right)^{-1}_{T,P},$$

or, introducing the notation

$$K_M = \frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_{M,T}, \quad h = \frac{1}{V}\left(\frac{\partial V}{\partial H}\right)_P \equiv \frac{\partial \omega}{\partial H}, \quad \chi_P \equiv \left(\frac{\partial M}{\partial H}\right)_{P,T},$$

we obtain for the isothermal compressibilities at constant M and H

$$K_M = K_H - h^2\chi_P^{-1}. \quad (2.7)$$

Similarly we obtain the following relation between the coefficients of volume expansion α_H and $\alpha_M \equiv (1/V)(\partial V/\partial T)_M$ at constant H and M:

$$\alpha_M = \alpha_H - \left(\frac{\partial M}{\partial T}\right)_P h\chi_P^{-1}, \quad (2.8)$$

and for the magnetic susceptibilities χ_V and χ_P at constant volume and pressure

$$\chi_V = \chi_P - h^2K_H^{-1}. \quad (2.9)$$

We also have the relation

$$\left(\frac{\partial M}{\partial T}\right)_V = \left(\frac{\partial M}{\partial T}\right)_P - h\alpha_H K_H^{-1}. \quad (2.10)$$

Using (2.7)–(2.10) and introducing the notation $B_{H,M} \equiv K^{-1}_{H,M}$, where B is the bulk modulus, we obtain the relations

$$B_H = B_M(1 - h^2\chi_P^{-1}B_H), \quad \chi_P B_H = \chi_V B_M,$$

$$\alpha_H = \left[\alpha_M + h\chi_P^{-1}\left(\frac{\partial M}{\partial P}\right)_V\right](1 - h^2\chi_P^{-1}B_H)^{-1}. \quad (2.11)$$

It is evident from (2.11) that when $h^2\chi_P^{-1}B_H = 1$, the quantities K_H, α_H, and χ_P are infinite. The resulting instability means that a homogeneous state cannot exist. The physical meaning of this instability will be discussed later. The thermodynamic relations in the form (2.7)–(2.11) have been discussed in detail by Shimizu.[6] He noted that it is necessary to distinguish between B_H and B_M, between χ_P and χ_V, and between α_H and α_M. Unfortunately, this is not done in most papers on Invars. In our opinion, a correctly formulated theory of the magnetovolume interaction must give results that are consistent with the thermodynamic approach.

The above relations, in spite of their great generality (they do not depend on the specific model of the ferromagnet) are incomplete, because they do not take into account the anisotropy in the elastic and magnetic properties of real Invar alloys. This deficiency can be overcome by replacing in (2.1)–(2.3) the volume V with the deformation tensor u_{ik} and the scalars M and H with the three-dimensional vectors M_i and H_i. However, we choose a different method based on the dependence of the thermodynamic potential of the ferromagnet on the deformations.[4–6] The elastic subsystem of the ferromagnet is treated in the harmonic approximation (a more general approach is possible). The thermodynamic potential of the magnetic subsystem is written in such a way that the ferromagnetic–paramagnetic phase transition can be considered. The explicit form of the MVI terms is deter-

mined from symmetry considerations, by experiments, or by the choice of a particular model for the ferromagnet.

3. THERMODYNAMIC POTENTIAL OF A FERROMAGNET WITH MAGNETOVOLUME INTERACTIONS AND THE EQUATION OF STATE

The thermodynamic potential of the ferromagnet is written as a sum of the exchange interaction energy, the elastic energy, the energy associated with external magnetic and elastic fields, and the MVI energy. First and second-order (in the deformations) magnetovolume interactions are taken into account. The first-order MVI has the usual form given in Refs. 4 and 5, for example. The second-order interaction depends on both volume and shear deformations. The necessity of including this interaction follows from the experiments and analysis of Haush.[14] The discussion of this Section is based on the results of Refs. 15 and 16.

The thermodynamic potential is written in the form

$$\Phi = \varphi(M^2) - MH + \frac{1}{2} c^0_{iklm} u_{ik} u_{lm}$$

$$- \sigma_{ik} u_{ik} + \gamma_{ik} u_{ik} M^2 + \frac{1}{2} \varepsilon_{iklm} u_{ik} u_{lm} M^2; \qquad (3.1)$$

where $\varphi(M^2)$ is the exchange energy, c^0_{iklm} and σ_{ik} are the elastic tensor without magnetovolume interactions and the external stress tensor, respectively; γ_{ik} and ε_{iklm} are the first and second-order MVI constants, respectively.

We do not include the magnetic crystal anisotropy energy since for Invars it is much smaller than the MVI energy. The fifth term in (3.1) is obtained from the general expression for the magnetoelastic interaction energy $\gamma_{iklm} u_{ik} M_l M_m$ (Ref. 17) by identifying the terms involving pure volume deformations, i.e. by putting $i = k$ in the general expression. It automatically follows that the MVI energy depends only on the magnitude of the magnetization, and not on its direction. We assume that $\mathbf{M} \| \mathbf{H}$. The effect of the anisotropy in the magnetic properties will be discussed in the Section devoted to fluctuation corrections.

The equilibrium equations of state are such that the thermodynamic potential is a minimum with respect to M and u_{ik}:

$$H = 2M\varphi'(M^2) + 2M\gamma_{ik} u_{ik} + M\varepsilon_{iklm} u_{ik} u_{lm},$$

$$\sigma_{ik} = c^0_{iklm} u_{lm} + \gamma_{ik} M^2 + \varepsilon_{iklm} M^2. \qquad (3.2)$$

A summation from 1 to 3 is understood over repeating Latin indices. The symmetry properties of the tensor ε_{iklm} are the same as those of c^0_{iklm}. We will consider the case of a cubic crystal, for which $\gamma_{ik} = \gamma\delta_{ik}$.

When $\sigma_{ik} = 0$ the second equation in (3.2) gives the spontaneous equilibrium spontaneous deformations u^0_{lm} as

$$(c^0_{iklm} + \varepsilon_{iklm} M^2) u^0_{lm} = -\gamma_{ik} M^2. \qquad (3.3)$$

Taking into account the thermoelastic term $\alpha_{ik} u_{ik} TB_0$ in the thermodynamic potential (see Ref. 17b, for example), where $\alpha_{ik} = \alpha\delta_{ik}$ is the coefficient of thermal expansion, (3.3) takes the form

$$(c^0_{iklm} + \varepsilon_{iklm} M^2) u^0_{lm} = -\gamma_{ik} M^2 + \alpha_{ik} TB_0. \qquad (3.4)$$

When $\gamma < 0$ the first term in (3.4) decreases with increasing temperature, while the second term increases. Hence the two terms can cancel and low thermal expansion is the basic characteristic of industrial Invar alloys. This is only one of the obvious consequences of magnetovolume interactions. We will attempt to show that if the magnetovolume interaction is large enough it can lead to a fundamental change in the equilibrium and dynamical properties of the ferromagnet.

We see from (3.4) that γ plays the role of a "magnetic expansion" constant and the ε_{iklm} resemble "magnetic elastic constants".

It follows from (3.3) that

$$u^0_{ik} = -\frac{1}{3} \gamma M^2 B_M^{-1} \delta_{ik}, \quad B_M = \frac{1}{3} [c^0_{11} + 2c^0_{12} + (\varepsilon_{11} + 2\varepsilon_{12}) M^2],$$

and the spontaneous magnetovolume deformation is

$$\omega \equiv u^0_{ii} = -\gamma M^2 B_M^{-1}. \qquad (3.5)$$

Differentiating the system of equations (3.2) with respect to H with $u_{ik} = \text{const}$, we obtain the following expression for the longitudinal magnetic susceptibility at constant volume χ_V:

$$\chi_V = [2\varphi'(M^2) + 4M^2\varphi''(M^2) + 2\gamma_{ik} u^0_{ik} + \varepsilon_{iklm} u^0_{ik} u^0_{lm}]^{-1}. \qquad (3.6)$$

Differentiating (3.2) with respect to H with $\sigma_{ik} = \text{const}$, we obtain a system of linear equations for the susceptibility at constant pressure χ_P and the induced magnetostriction $\partial u_{ik}/\partial H$:

$$c^M_{iklm} \frac{\partial u_{lm}}{\partial H} = -2M\Gamma_{ik}\chi_P,$$

$$\chi_V^{-1}\chi_P + 2M\Gamma_{ik} \frac{\partial u_{ik}}{\partial H} = 1, \quad \Gamma_{ik} = (\gamma_{ik} + \varepsilon_{iklm} u^0_{lm}). \qquad (3.7)$$

Similarly, it can be shown that the elastic constants $c^H_{iklm} = (\partial\sigma_{ik}/\partial u_{lm})_H$ and $c^M_{iklm} = (\partial\sigma_{ik}/\partial u_{lm})_M$ are

$$c^H_{iklm} = c^M_{iklm} - 4M^2\chi_V\Gamma_{ik}\Gamma_{lm}, \quad c^M_{iklm} = c^0_{iklm} + \varepsilon_{iklm} M^2. \qquad (3.8)$$

We obtain from the first equation of (3.2)

$$\chi_V^{-1} \frac{\partial M}{\partial \sigma_{lm}} = 2M\Gamma_{ik} s^H_{iklm}, \qquad (3.9)$$

where

$$s^H_{iklm} = \left(\frac{\partial u_{ik}}{\partial \sigma_{lm}}\right)_H.$$

Using (3.6)–(3.9), we obtain the following relations, which will be needed in comparing the theoretical and experimental results:

$$\frac{\partial\omega}{\partial H} = -2M\gamma\chi_P B_M^{-1} \text{ при } \sigma_{ik} = -P\delta_{ik}, \quad \frac{\partial M}{\partial P} = 2M\gamma\chi_V B_H^{-1},$$

$$B_H = B_M(1 - 4\gamma^2 M^2 \chi_V B_M^{-1}), \quad \chi_P^{-1} = \chi_V^{-1} - 4\gamma^2 M^2 K_M, \qquad (3.10)$$

$$\alpha_H = \alpha_M - 2\gamma M B_M^{-1} \left(\frac{\partial M}{\partial T}\right)_P.$$

These relations are consistent with (2.7)–(2.11), since $h^2\chi_P^{-1} B_H = 4\gamma^2 M^2 \chi_V B_M^{-1}$. It is not difficult to show from (3.10) that the relation (2.4) is also satisfied. It is assumed in (3.10) that $\Gamma_{ik} = \gamma[1 - (\varepsilon_{11} + 2\varepsilon_{12}) M^2 (3B_M)^{-1}]$

$\delta_{ik} \simeq \gamma\delta_{ik}$. It will be shown below that this relation is satisfied to within a few percent.

The expressions for the susceptibilities and the compressibilities

$$\chi_P^{-1} = \chi_V^{-1} - 4\gamma^2 M^2 K_M, \quad K_H^{-1} = K_M^{-1} - 4\gamma^2 M^2 \chi_V,$$
$$\chi_V^{-1} = \chi_0^{-1} - 2\gamma^2 M^2 K_M,$$

where χ_0 is the longitudinal susceptibility without magnetovolume interaction (which can be obtained from (3.6) by putting $\gamma = 0$ and $\varepsilon_{iklm} = 0$) resemble the formulas for the Green's function in field theory[17c] and represent a renormalization of the thermodynamic quantities because of magnetovolume interactions. The renormalization results from the change in the ground state of the magnetic and elastic subsystems of the material due to magnetovolume interactions. It will be shown below that fluctuations in the magnetic and elastic subsystems (phonons, magnons, and so forth) lead to additional changes in the thermodynamic quantities.

Numerical estimates show why magneto-volume interactions must be taken into account in real ferromagnets. We consider mainly Fe–Ni and Fe–Pt alloys, since they have been extensively studied experimentally and show the largest magnetovolume effects.

The following experimental quantities are known for the disordered alloy $Fe_{65}Ni_{35}$ (Ref. 18): $\omega(0\ ^\circ K) = 1.9\cdot 10^{-2}$, $M(0\ ^\circ K) = 1.55\cdot 10^6 A/m = 1.55\cdot 10^3 erg/G\cdot cm^3$, $B_M(0\ ^\circ K) \approx 2\cdot 10^{12}$ erg/cm^3 $= 2\cdot 10^{11}$ N/m^2, $T_c = 500\ ^\circ K$. The MVI constant is found from the experimental value of $\omega(0\ ^\circ K)$ using (3.5). We obtain $\gamma \approx -1.6\cdot 10^4\ G^2 cm^3/erg = -1.6\cdot 10^{-3}\ N/A^2$. Similar estimates can be found in Ref. 4a, Ch. IV. The second-order MVI constants are found following Ref. 11 and are equal to $\varepsilon_{11} \approx -2.5\cdot 10^4\ G^2/erg\cdot cm^{-3}$, $\varepsilon_{12} \approx 10^5\ G^2\ cm^3/erg$, $\varepsilon_{44} \approx -6\cdot 10^4$.

The longitudinal magnetic susceptbilities χ_P and χ_V in (3.10) are difficult to determine in terms of the experimental high-field susceptibility (the susceptibility near technical saturation) since this susceptibility is the sum of longitudinal and transverse terms. We determine χ_P and χ_V using the experimental value of the induced volume magnetostriction $\partial\omega/\partial H$. Then χ_P can be found from (3.10), since the other quantities in this equation are known. For Fe–Ni Invar at 300 °K we have $\chi_P \approx 6.8\cdot 10^{-4}$ erg/G·cm^3 and $\chi_V \approx 4.3\cdot 10^{-4}$. We note that $\chi_{expt} \approx 13\cdot 10^{-4}$. Then

$$B_M - B_H = 4\gamma^2 \chi_V M^2 \approx 5{,}2\cdot 10^{11}\ erg/cm^3,$$

which agrees fairly well with the experimental value of $\sim 6\cdot 10^{11}$ erg/cm^3 (see Ref. 16, for example). From the experimental data of Ref. 18 (see also Ref. 4a, Ch. IV) we have

$$M^{-1}\frac{\partial M}{\partial T} \equiv \frac{\partial \sigma}{\partial T} \approx -10^{-3}(deg)^{-1},$$
$$\alpha_H - \alpha_M = 2\gamma M B_M^{-1}\left(\frac{\partial M}{\partial T}\right)_p \approx 3\cdot 10^{-5}\ (deg)^{-1},$$
$$(\alpha_H - \alpha_M)_{expt} = 4{,}0\cdot 10^{-5}(deg)^{-1}.$$

We see that the estimated value of χ_P is half as large as χ_{expt}. The cause of this disagreement has already been discussed briefly. We will return to this question, as well as a more detailed comparison with experiment.

For the disordered alloy $Fe_{72}Pt_{28}$ we have the experimental values:[20] $\omega(0) = 1.6\cdot 10^{-2}$, $M_0(0°K) = 1.5\cdot 10^3$ erg/G·cm^3 $= 1.5\cdot 10^6$ A/m, $B_M(0\ °K) = 1.8\cdot 10^{12}$ dyn/cm^2, $T_c = 380\ °K$. Using the procedure for Fe–Ni, we obtain $\gamma \approx -1.3\cdot 10^4\ G\cdot cm^3/erg$. In the same units we have $\varepsilon_{11} \approx -7.4\cdot 10^4$, $\varepsilon_{12} \approx 1.8\cdot 10^5$, $\varepsilon_{44} \approx -10^5$. These values of the MVI constants result in satisfactory agreement between the experimental and calculated values of the shear modulus, bulk modulus, and coefficient of thermal expansion. It follows from these numerical values that for Invars the MVI energy is $\gamma M^2\omega \approx 5\cdot 10^8$ erg/cm^3, or about 10% of the energy of the exchange interaction.

Hence it is evident that the phenomenological theory of magnetovolume interactions can provide a satisfactory quantitative description of the thermodynamic properties in Invars. The connection between the electronic structure and the large magnetovolume effect in ferromagnets and the calculation of the values of the MVI constants are questions left to the microscopic theory.

We have discussed far from all of the consequences of magnetovolume interactions. To make further progress, we consider the magnetovolume interaction in the molecular field approximation for the Heisenberg model. We note that magnetovolume effects have been considered by many authors using various models of ferromagnets.[8,9,12,13] Without considering the merits and deficiencies of these papers we note, following Shimizu,[6] that not all of their results are consistent with the rigorous thermodynamic approach discussed above.

4. MAGNETOELASTIC INTERACTION IN THE MEAN-FIELD APPROXIMATION FOR THE HEISENBERG MODEL

In spite of the fact that most Invars and Elinvars are compounds of 3*d*-metals and hence the applicability of the Heisenberg model is questionable, a large number of properties can be calculated using this model over a wide temperature region and the overall effects of magnetovolume interactions can be discussed. In addition, it will be shown that the main consequences of magnetovolume interactions do not depend on the model of the ferromagnet. Only the quantities determining the magnetic properties (such as $M(T)$, χ, T_c, and so on) depend on the model.

Following Ref. 19, we consider the dependence of the exchange integral on the deformations:

$$J = J_0 + \gamma_{ik}^* u_{ik} + \frac{1}{2}\varepsilon_{iklm}^* u_{ik} u_{lm} \qquad (4.1)$$

where γ_{ik}^* and ε_{iklm}^* are the first and second-order MVI tensors. Below we will establish a connection between these quantities and the tensors γ_{ik} and ε_{iklm} introduced earlier.

In the Heisenberg model γ_{ik}^* are the first derivatives of the exchange integral with respect to the deformations and ε_{iklm}^* are linear combinations of the first and second derivatives. If we had started from the model of collective electrons, the MVI constants would have been determined by the deformation dependence of the parameters of the electronic structure, such as the density of states and the electron-electron interaction constants.[56] At the present time it is not possible to calculate the values of the MVI constants or to determine the features of the electronic structure responsible for the large values of the MVI constants, although

such a calculation was attempted in Ref. 9 and the value of γ was obtained to within an order of magnitude.

The thermodynamic potential per unit volume of the ferromagnet is written in the form

$$\Phi = F_m + \frac{1}{2} c^0_{iklm} u_{ik} u_{lm} - \sigma_{ik} u_{ik}, \tag{4.2}$$

where

$$F_m = nzJs^2m^2 - nk_B \ln\left[\operatorname{sh}\frac{2s+1}{s}\left(h + h_E m\right)\left(\operatorname{sh}\frac{h+h_E m}{2s}\right)^{-1}\right]$$

is the free energy of the magnetic subsystem with the exchange integral given by (4.1); n is the number of atoms per unit volume, z is the number of nearest neighbors, s is the spin, m is the reduced magnetization, $h = 2\mu\ sH/k_BT$, $h_E = 2\mu s H_E/k_BT$, $H_E = Js/\mu$, H is the external magnetic field and μ is the Bohr magneton. Our calculation is essentially a generalization of the Bean–Rodbell model[21] to the case of arbitrary spin and nonlinear dependence of the exchange integral on distance. In the theory of phase transitions[22] a similar approach for Ising spins is known as the Kittel model.

Minimizing the thermodynamic potential with respect to m and u_{ik}, we obtain coupled equations of state for the magnetic and elastic subsystems:

$$\begin{aligned} &m = B_s(x), \quad x = (2\mu sH + 2zs^2Jm)(k_BT)^{-1}, \\ &(c^0_{iklm} - nzs^2m^2\varepsilon^*_{iklm})u_{ik} = nzs^2m^2\gamma^*_{ik} + \sigma_{ik}; \end{aligned} \tag{4.3}$$

where $B_s(x)$ is the Brillouin function.

The nondeformed state is defined to be the unstressed ($\sigma_{ik} = 0$) paramagnetic ($m = 0$) state at arbitrary temperature, since we have neglected thermal expansion.

The equations of state (4.3) are analogous to (3.2) and determine all equilibrium properties of the ferromagnet. Taking u_{ik} from (4.3) and putting it into (4.2), we obtain that the exchange integral J is renormalized because of magnetovolume interactions and depends on the magnetization and external stresses. The molecular field H_E will then be a nonlinear function of the magnetization, and so under certain conditions the magnetic phase transition can change from second order to first order. The magnetization and Curie termperature depend on the external stresses.

Differentiating (4.3) with respect to $u_{ik} = 0$ with $H = \text{const}$, we obtain an equation for the elastic constants

$$c^H_{iklm} = c^0_{iklm} - nzs^2m^2\varepsilon^*_{iklm} - \frac{s^2z^2}{\mu^2} m^2\chi_V\Gamma^*_{ik}\Gamma^*_{lm}; \tag{4.4}$$

where $\Gamma^*_{ik} = (\gamma^*_{ik} + \varepsilon^*_{iklm}u_{lm})$ and the magnetic susceptibility at constant volume χ_V is determined later. To obtain c^*_{iklm} as functions of m, σ_{ik}, and T, we substitute u_{ik} from (4.3) into (4.4). The elastic constants c^H_{ik} depend on the stresses directly, and also indirectly through the magnetization. Hence the magnetovolume interaction leads to effective anharmonicity.

When $m = \text{const}$ the elastic constants are equal to

$$c^M_{iklm} = c^0_{iklm} - nzs^2m^2\varepsilon^*_{iklm}. \tag{4.5}$$

Comparing (4.4) and (4.5) with (3.8), it is evident that they are identical if

$$\gamma^*_{ik} = -\frac{4\mu^2 n}{z}\gamma_{ik}, \quad \varepsilon^*_{iklm} = -\frac{4\mu^2 n}{z}\varepsilon_{iklm}, \quad M = 2\mu snm. \tag{4.6}$$

Since $\gamma^*_{ik} = \partial J/\partial u_{ik} = a(\partial J/\partial a)\delta_{ik}$, we obtain an explicit expression for the MVI constant γ in terms of the derivative of the exchange integral with respect to the coordinate:

$$\gamma = -\frac{za}{4\mu^2 n}\frac{\partial J}{\partial a}. \tag{4.7}$$

The spontaneous volume magnetostriction ω is, from (4.3) with $\sigma_{ik} = 0$

$$\omega = nzs^2\gamma^* B_M^{-1} m^2,$$

which reduces to (3.5), if we use (4.6).

Explicit expressions for the magnetic susceptibilities χ_V and χ_P follow from (4.3)

$$\chi_V = 2\mu sn\left(\frac{\partial m}{\partial H}\right)_V = 4\mu^2 s^2 n B_s'(x)(k_BT - 2zs^2JB_s'(x))^{-1}, \tag{4.8}$$

$$\chi_P = \chi_V\left(1 - \frac{\Gamma^2 m^2\chi_V}{2\mu sn}\right)^{-1}, \tag{4.9}$$

where

$$\Gamma^2 = 2z^2ns^3\mu^{-1}B_M^{-1}[\gamma^* + \tfrac{1}{3}(\varepsilon^*_{11} + 2\varepsilon^*_{12})\omega]^2.$$

Again it can be shown that (4.9) is identical to the corresponding expression from the preceding Section. The equations for $\partial\omega/\partial H$ and $\partial M/\partial P$ are also the same. This proves that the consequences of the magnetovolume interaction are independent of the model of the ferromagnet.

We did not take into account thermal expansion in (4.2). This can be done by adding a thermoelastic term of the form $B_0\ \alpha_{ik}u_{ik}T$, where $\alpha_{ik} = \alpha_0\ \delta_{ik}$. Here α_0 is the coefficient of volume expansion of the ferromagnet without magnetovolume interactions. Then the thermoelastic deformation term $B_0\ \alpha_{ik}T$ appears on the right hand side of the second equation of (4.3). Differentiating (4.3) with respect to T, we obtain an expression for the coefficient of linear expansion at constant H:

$$\alpha_H = \left(\alpha_0 - \frac{zsk_o T_c\gamma^*}{2\mu^2 TB_V}\chi_V m^2\right)\left(1 - \frac{\Gamma^2 m^2\chi_V}{2\mu sn}\right)^{-1}. \tag{4.10}$$

Comparing this expression with (2.11), we obtain a relation between $(\partial M/\partial T)_V$ and χ_V

$$\left(\frac{\partial M}{\partial T}\right)_V = -\frac{k_BT_c}{2\mu T}\chi_V m, \tag{4.11}$$

which is valid for our model (like (4.10)) at temperatures exceeding the Debye temperature θ_D.

Substituting u_{ik} from the second equation of (4.3) into the first, we obtain an expression for $m(T)$. From the high-temperature series expansion of the Brillouin function one can obtain an equation for T_c as a function of the external stresses σ_{lm}

$$T_c = \frac{2zs(s+1)}{3k_B}(J_0 + \gamma^*_{ik}s^0_{iklm}\sigma_{lm} + \frac{1}{2}\varepsilon^*_{iklm}s^0_{ikpn}\sigma_{pn}s^0_{lmrs}\sigma_{rs}); \tag{4.12}$$

where s^0_{iklm} are the elastic compliances.[23]

The dependence of the Curie temperature on pressure $\sigma_{ik} = -P\delta_{ik}$ has the form

$$T_c = T_c^0 - \frac{2zs(s+1)\gamma^*}{3k_B B_0} P + \frac{2zs(s+1)(\varepsilon_{11}^* + 2\varepsilon_{12}^*)}{18k_B B_0^2} P^2. \quad (4.13)$$

Substituting in (4.13) the values $\gamma^* \approx 3.6 \cdot 10^{-14}$ erg and $(\varepsilon_{11}^* + 2\varepsilon_{12}^*) \approx -3.8 \cdot 10^{-13}$ erg obtained with the help of (4.6) and the numerical values of γ and ε_{ik} for the iron-nickel alloy, and also $z = 12$ and $s = 1$, we obtain $\partial T_c/\partial P \simeq -3$ °K/kbar at a pressure of 10 kbar, which is consistent with the experimental data of 3–5 °K/kbar (Ref. 1). At $P \sim 10$ kbar the third term is only a few percent of the second. They are comparable for pressures of hundreds of kbar.

The dependence of T_c on the shear stresses can be obtained from (4.12). For example, for a torsion σ about the principal symmetry axis of a cubic crystal we have

$$T_c = T_c^0 + \frac{2zs(s+1)(\varepsilon_{11}^* - \varepsilon_{12}^*)}{k_B(c_{11}^0 - c_{12}^0)^2} \sigma^2. \quad (4.14)$$

Since $(\varepsilon_{11}^* - \varepsilon_{12}^*) > 0$ in Fe–Ni Invar, it follows that T_c increases with increasing σ.

Another consequence of magnetovolume interactions in ferromagnets is a change in the nature of the magnetic phase transition from second order to first order with an increase in the absolute value of the constant γ^*. An expression for the critical value γ_{cr}^* can be obtained by setting to zero the coefficient of m^3 in the high-temperature expansion of the Brillouin function. The coefficient of m must vanish simultaneously. In the absence of external pressure and assuming $s = 1$ we have

$$\gamma_{cr}^2 = \frac{9k_B T_c B_0}{32z^2 n}, \quad \text{or} \quad |\gamma_{cr}| = \frac{3}{16\sqrt{2}} \frac{(k_B T_c B_0)^{1/2}}{\mu^2 n^{3/2}}. \quad (4.15)$$

This is the condition for a tricritical point on the second-order phase transition curve.[24] If $\gamma^* < \gamma_{cr}^*$ the transition is second order and if $\gamma^* > \gamma_{cr}^*$ it is first order. This condition is correct in the mean-field theory. When fluctuations are taken into account a first-order transition is possible for small values of $(T - T_c)/T_c$ even when $\gamma^* < \gamma_{cr}^*$ (Ref. 25).

For example, for Fe–Ni Invar $\gamma_{cr}^* \simeq 4.9 \cdot 10^{-21}$ J, or $\gamma_{cr} \approx -2.1 \cdot 10^4$ G²cm³/erg. Comparing these values with the experimental value $|\gamma| \approx 1.6 \cdot 10^4$ in Fe–Ni Invar, it is evident that at zero pressure the magnetic phase transition should be second order and this is indeed the case.

When $\eta = 1 - h^2 \chi_P^{-1} B_H = 1 - \Gamma^2 m^2 \chi_V / 2\mu s n$ vanishes, it follows from (2.11) and (4.9) that χ_P, α_H, and B_H^{-1} diverge. Substituting in the above formula for η:

$$m^2 = \frac{8}{3} \frac{T_c - T}{T}, \quad \chi_V = \frac{4}{3} \frac{\mu^2 n}{k_B} (T_c - T)^{-1},$$

(which hold for $T \leqslant T_c$ and $s = 1$) and also Γ^2 from (4.9), we find that (4.15) follows from the condition $\eta = 0$ at $T = T_c$. Hence some of the thermodynamic quantities diverge at the tricritical point, as would be expected.

Although the magnetic phase transition in Fe–Ni and Fe–Pt Invars is second order in the absence of pressure, the transition can be changed to first order by applying pressure.[26] We calculate the magnetic phase diagrams of Fe–Ni and Fe–Pt Invars under pressure, using the MVI constants for these alloys.

It follows from (4.3) (compare with Ref. 27) that:

$$m = B_s(x), \quad x = \frac{2zs^2 Jm}{k_B T}; \quad (4.16)$$

here J depends on the deformations (see (4.1)).

It should be noted that a pressure-induced change in the phase transition from second order to first order does not follow from the thermodynamic potential (3.1) given in the preceding Section. To obtain this conclusion magnetovolume interactions must be taken into account more systematically in (3.1). At low pressures ~ 10 kbar the results of the preceding and current Sections are the same. (If $\gamma^* < 0$ an applied pressure can change a first-order magnetic phase transition to a continuous (i.e. a second-order) transition.[25])

The deformation tensor in the case of spontaneous magnetovolume deformation and uniform compression has the form

$$u_{ik} = (nzs^2\gamma^* m^2 - P)(3B_M)^{-1}\delta_{ik}. \quad (4.17)$$

To construct the phase diagram it is sufficient to keep terms up to fifth order in m in the equation of state (4.16). Substituting (4.17) into (4.1) and then into (4.16) and expanding the Brillouin function and the coefficients depending on m in power series in the magnetization, we obtain the equation of state in the form

$$Am + Bm^3 + Cm^5 = 0; \quad (4.18)$$

where $A = (T - T_c(P))/T$ with $T_c(P)$ is given by (4.13), and B and C are functions of temperature and pressure.

At low pressure $B > 0$ and the second-order phase transition curve is given by the condition $A = 0$. The tricritical point is obtained by solving the equations $A = 0$ and $B = 0$ simultaneously. In the region $B < 0$, $C > 0$ the first-order phase transition line and the spinodals of the magnetic ($m \neq 0$) and nonmagnetic ($m = 0$) phases are determined by the equations $A = (3/16)B^2/C$, $A = (1/4)B^2/C$, and $A = 0$, respectively.

The phase diagram of the disordered alloy $Fe_{72}Pt_{28}$ shown in Fig. 1 was calculated using the experimental values of the MVI constants. The phase diagram for $Fe_{65}Ni_{35}$ is not given, since it differs only slightly from the diagram shown in Fig. 1. For Fe–Ni Invar we have $T_3 = 322$ °K and $P_3 = 61$ kbar.

We note the relatively small temperature hysteresis in the first-order phase transition region of Fig. 1. The magnitude of the hysteresis is defined to be the temperature difference between the spinodals of the magnetic and nonmagnetic phases at constant P.

These results show the important influence of the second-order MVI constants on the position of the tricritical point and on the phase diagram as a whole. Without the second-order constants ($\varepsilon_{11}^* = \varepsilon_{12}^* = 0$) the coordinates of the tricritical point would be $T_3 = 145$ °K, $P_3 = 61$ kbar for $Fe_{72}Pt_{28}$ and $T_3 = 250$ °K, $P_3 = 84$ kbar for $Fe_{65}Ni_{35}$. The second-order MVI constants shift the tricritical point toward lower pressure and lead to another tricritical point in the negative pressure region. Its coordinates are $P_3 = -470$ kbar, $T_3 = 320$ °K for $Fe_{72}Pt_{28}$; it is apparently

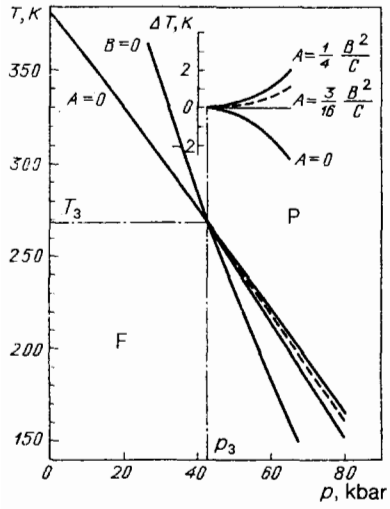

FIG. 1. Magnetic phase diagram of the disordered alloy $Fe_{72}Pt_{28}$ under pressure.[27]

only of academic interest. The large effect of the second-order MVI constants in the phase diagram is another demonstration of the importance of the second-order magnetovolume interaction for Invar anomalies.

We have given a detailed discussion of the effect of the second-order magnetovolume interactions because they are not nearly so well known as the first-order magnetovolume interaction. The constants ε_{ik}^{*} determine the temperature dependence of the shear elastic constants $c_{11}-c_{12}$ and c_{44}. Second-order magnetoelastic interactions also lead to a nonlinear dependence of T_c on applied stress (see (4.13) and (4.14)). Second-order magnetovolume interactions affect the other properties only slightly. Hence they will sometimes be neglected in the discussion below in order to simplify the presentation.

5. MAGNETOVOLUME INTERACTIONS AND THE EFFECT OF PHONONS ON THE MAGNETIC PROPERTIES IN WEAK COLLECTIVE FERROMAGNETS

In this Section we consider the effect of magnetovolume interactions on the thermodynamic properties of weak ferromagnets. In contrast to the preceding Sections, the effect of thermal phonons is taken into account. Thermal phonons are really outside the framework of the harmonic approximation for the elastic subsystem because they cause the Debye temperature θ_D to depend on volume. The effect of phonons on the magnetic properties was considered in Refs. 12 and 13 by assuming that the elastic constants and Debye temperature depend on magnetization. Using this assumption, it was concluded in Refs. 12 and 13 that phonons have a significant effect on the magnetic properties. In our view, phonons determine the temperature dependence of the magnetization, lead to the Curie–Weiss law in collective magnets, and may explain the Invar effect. Even if the mechanism proposed in Refs. 12 and 13 is correct, for which there is insufficient experimental proof in our opinion, there is another way of taking into account the effect of phonons on the magnetic properties. The method discussed below is consistent with the results presented earlier, unlike the method of Refs. 12 and 13. A similar calculation for the Heisenberg model was given in Ref. 10.

We consider a weak collective magnet for which the thermodynamic potential can be written in the form

$$\Phi = \frac{1}{2}a_0M^2 + \frac{1}{4}b_0M^4 + \frac{1}{2}B_0\omega^2 - P\omega + 3nk_B\theta(V)f\left(\frac{T}{\theta(V)}\right) + \gamma\omega M^2 - HM; \qquad (5.1)$$

here $V = V_0(1+\omega)$, $a_0 = \chi^{-1}(0)(T_0^2 - T^2)/T_0^2$, $\chi^{-1}(0) = \chi_M^{-1} - \lambda$; $\chi_P = 2\mu^2N_Fn$ is the one-particle Pauli susceptibility, N_F is the density of states on the Fermi level; $b_0 = b_0(0)(1+gT^2)$, $b_0(0) = (\mu^2/2\chi_{th}^3)[N_F'/N_F)^2 - (N_F''/3N_F)]$; $T_0 = T_F(\lambda\chi_{th}-1)^{1/2}$, γ is the MVI constant and can be expressed in terms of the parameters of the band structure.[5] The term proportional to $\theta f(T/\theta)$ is the phonon contribution of the corresponding Grüneisen states, V_0 is the volume at $T=0$, $M=0$ and without anharmonic effects. The rest of the notation is the same as in Ref. 28. To simplify the discussion, we have neglected second-order magnetovolume interactions in (5.1).

Since $\theta(V) = \theta_0(1-\Gamma\omega)$, where $\Gamma = -\partial\ln\theta/\partial\ln v$ is Grüneisen's constant, by minimizing (5.1) with respect to M and ω we obtain the equilibrium equations of state:

$$H = a_0M + b_0M^3 + 2\gamma\omega M,$$
$$\omega = -\left(\gamma M^2 + P - 3nk_B\theta_0\Gamma\varphi\left(\frac{T}{\theta_0}\right)\right)B_0^{-1}. \qquad (5.2)$$

Here $\varphi(x) = f(x) - xf'(x)$, $b_0 > 0$.

Substituting ω from the second equation into the first, we obtain

$$H = aM + bM^3, \qquad (5.3)$$

where $a = a_0 - 2\gamma B_0^{-1}P + 6\gamma nk_5\theta_0\Gamma\varphi(T/\theta_0)$, $b = b_0 - 2\gamma^2B_0^{-1}$. The main difference between (5.3) and the results of Refs. 12 and 13 is that there the renormalization of the coefficient b_0 was not taken into account, while the renormalization in a was determined by a different interaction constant. In addition, the dependence of θ on M was postulated *a priori*, in Refs. 12 and 13 whereas here it is determined by the interaction. The dependence $\theta(M)$ becomes obvious if we substitute the equilibrium value of ω from (5.2) into $\theta(\omega)$.

The renormalizations of the magnetic properties described above originate from changes in the equilibrium volume of the ferromagnet caused by spontaneous volume magnetostriction, external pressure, zero-point vibrations, and thermally excited phonons.

We write down the following expressions for the physical quantities in the ferromagnetic state:

$$a(0) = \chi_{th}^{-1} - \lambda + 6\gamma nk_B\theta_0B_0^{-1}\Gamma f(0) - 2\gamma B_0^{-1}P, \quad M^2 = -a/b,$$
$$\chi_V^{-1} = 2b_0M^2, \quad \chi_P^{-1} = 2bM^2, \quad B_H = B_0 - 4\gamma^2M^2\chi_V, \qquad (5.4)$$
$$\frac{b}{b_0} = 1 - 4\gamma^2M^2\chi_VB_0^{-1}.$$

Comparing (5.4), (3.10), and (4.9), we can show once again that the consequences of the magnetovolume interaction are independent of the model of the ferromagnet. Because $\gamma < 0$ for many weak ferromagnets and $n \sim 10^{23}$ cm^{-3}, $\theta \sim 3\cdot 10^2$ °K; $|\gamma B_0^{-1}| \sim 10^{-8}$G^2(cm^3/erg)^2; $\Gamma f(0) \sim 1$, then

for $\chi(0) \sim 10^{-3}$–10^{-4} the increase in $\chi_P^{-1}(0)$ and $M(0)$ because of zero-point vibrations is 1–10%. The difference between b_0 and b is estimated to be only a fraction of a percent for weak ferromagnets, whereas for Fe–Ni and Fe–Pt Invars[16] this difference reaches several dozen percent.

For $P = 0$ and nonzero temperature

$$a(T) = \chi^{-1}(0)\left(1 - \frac{T^2}{T_0^2}\right) - 6\gamma n k_B \theta_0 B_0^{-1} \Gamma \varphi\left(\frac{T}{\theta_0}\right). \qquad (5.5)$$

When $T < \theta$ we have $\varphi(T/\theta) = (\pi^4/5)(T/\theta)^4$ and the condition $a = 0$ determining the Curie temperature T_c takes the form

$$1 - \frac{T^2}{T_0^2} - \frac{T^4}{T_1^4} = 0, \quad T_1 = \theta\left(\frac{5B_0}{6\pi^4 n\gamma k_B \theta_0 \Gamma}\right)^{1/4}. \qquad (5.6)$$

Recall that T_0 determines the contribution of Stoner excitations. When $T > \theta$ we have $\varphi(T/\theta) = T/\theta$ and T_c is given by the equation

$$1 - \frac{T^2}{T_0^2} - \frac{T}{T_2} = 0; \quad T_2 = (6nk_B \Gamma\gamma\chi(0))^{-1} B_0. \qquad (5.7)$$

In (5.6) and (5.7) $T_c = T_0$ if $T_1(T_2) \gg T_0$ and $T_c = T_1(T_2)$ when $T_0 \gg T_1(T_2)$. Numerical estimates give $T_1 \sim \theta \sim T_0$ and $T_2 \sim 10^4$ °K for $\chi(0) \sim 10^{-4}$. In most very weak ferromagnets $T_c \ll T_0$ and so for the mechanism considered here, phonons do not have an important effect on the temperature dependence of the magnetization and the susceptibility of a ferromagnet. This conclusion contradicts the assertions of Refs. 12 and 13.

Assuming[29] that T_c of a weak ferromagnet is given by (5.6), but with T_0 replaced by T_{0c}, where T_{0c} is the temperature typical of spin fluctuations ($T_{0c} \ll T_0$), we obtain the following expression for the dependence of T_c on atomic mass m (the isotope effect):

$$\frac{d \ln T_c}{d \ln m} = -\frac{1}{2}\frac{d \ln T_c}{d \ln \theta} \simeq \frac{3}{4}\left(\frac{T_c}{T_1}\right)^4 \sim 10^{-3}.$$

This value is not inconsistent with experiment for $ZrZn_2$ (Ref. 30). When $T_c \sim T_1$ the phonon mechanism determines T_c and

$$\frac{d \ln T_c}{d \ln m} \sim 1.$$

Hence in our approach phonons do not have an important effect on the magnetic properties of a ferromagnet, although in some cases (large compressibility, strong anharmonicity) they can facilitate the onset of temperature-induced ferromagnetism and then they significantly ($\sim 10\%$) affect the magnetic properties. For weak collective ferromagnets like MnSi and $ZrZn_2$ we have $4M^2\gamma^2\chi B_0^{-1} \sim 10^{-2}$–$10^{-3}$, while the differences between B_H and B_M, χ_P and χ_V, and b and b_0 are less than a percent. In Fe–Ni and Fe–Pt Invars $4M^2\gamma^2\chi B_0^{-1} \sim 1$ and the above quantities differ by several dozen percent. Note that in spite of the same value of the MVI constant γ in weak ferromagnets and in Fe–Ni Invar, their magnetizations differ by nearly two orders of magnitude. Therefore in order for the effect of magnetovolume interactions to be large, we need a magnetization of order $M \sim 10^3$ G, in addition to having $\gamma \sim 10^4$.

Finally, we consider the coefficient of thermal expansion. According to (5.2) $\alpha_H = \partial\omega/\partial T$ is given by

$$\alpha_H = 3nk_B \Gamma B_M^{-1} \varphi'(T/\theta) - 2\gamma M B_M^{-1}\left(\frac{\partial M}{\partial T}\right)_P$$

$$\equiv \Gamma_\Phi B_M^{-1} c_\Phi - 2\gamma M B_M^{-1}\left(\frac{\partial M}{\partial T}\right)_P; \qquad (5.8)$$

c_{ph} is the phonon part of the heat capacity. Generalizing this expression by taking into account thermal excitations in the electronic subsystem and magnetic fluctuations, we can write

$$\alpha_H = \alpha_M - 2\gamma M B_M^{-1}\left(\frac{\partial M}{\partial T}\right)_P,$$

$$\alpha_M = \Gamma_e B_M^{-1} c_e + \Gamma_M B_M^{-1} c_M + \Gamma_{ph} B_M^{-1} c_{ph}, \qquad (5.9)$$

where c_e, c_m and Γ_e, Γ_m are the electronic and magnetic heat capacities and Grüneisen constants, respectively.

It follows from (5.9) that there are two magnetic contributions to the coefficient of volume expansion. One (the last term in (5.9)) is due to the renormalization of the ground state, i.e. spontaneous volume magnetostriction, while the second (proportional to the magnetic heat capacity) is due to the renormalization of the excited states.

A similar expression, but without the last term, was discussed in Ref. 10 for the Heisenberg model. In this model

$$\Gamma_M = -\frac{d \ln J}{d \ln V} = -\frac{\gamma^*}{3J}.$$

Hence when $\gamma < 0$ both magnetic contributions are negative, which may explain the negative value of the coefficient of thermal expansion in weak collective ferromagnets and in many Invar alloys at low temperature.[1] The equation (5.9) is an attempt to take into account the effect of fluctuations on a thermodynamic property.

6. FORMULATION OF THE THEORY OF MAGNETOVOLUME INTERACTIONS AS A PROBLEM OF INTERACTING FIELDS IN CLASSICAL FIELD THEORY

The phenomenological theory of magnetovolume interactions discussed above can be used to explain the equilibrium thermodynamic properties of Invars. The anomalies of the physical quantities discussed above were associated with the renormalization of the ground state, i.e. with nonzero spontaneous magnetization M_0 and spontaneous volume magnetostriction.

To discuss dynamical effects such as the propagation of spin waves and acoustic waves, and also the effect of fluctuations (phonons, magnons, and so forth) on the thermodynamic properties, we consider the problem of magnetovolume interactions in the spirit of the theory of interacting fields, i.e. we consider $M(\mathbf{x},t)$ and $u_{ik}(\mathbf{x},t)$ as functions of the spatial coordinates $\mathbf{x}$ and the time t.

From the equations of motion for $M(\mathbf{x},t)$ and $u_{ik}(\mathbf{x},t)$ we will find that the magnetovolume interaction modifies the dispersion of spin and acoustic waves and leads to attenuation. In addition, it will be shown that magnetovolume interactions lead to nonlinear effects in both the elastic and magnetic subsystems of the ferromagnet (anharmonicity of

magnetoelastic origin and nonlinear parametric resonance in the spin system). We will consider the effect of magnetic fluctuations on the thermodynamic properties, which lead to magnetic contributions to the coefficient of linear expansion and to the compressibility above T_c. It was shown above that in the mean-field approximation the MVI problem can be solved exactly. When fluctuations are included, however, it is necessary to resort to an approximate treatment.

The thermodynamic potential in this case will have the form[31]

$$F = \frac{1}{V}\int \phi\left[M(\mathbf{x});\ u_{ik}(\mathbf{x});\ \frac{\partial M_i}{\partial x_j}\right] dV. \tag{6.1}$$

where the thermodynamic potential density ϕ is

$$\phi = \varphi(M^2) + \frac{1}{2}\alpha_0\left(\frac{\partial \mathbf{M}}{\partial x_j}\right)^2 + \frac{1}{2}c^0_{iklm}u_{ik}u_{lm} + \gamma u_{ik}\delta_{ik}M^2$$
$$+ \frac{1}{2}\gamma' u_{ik}\delta_{ik}\left(\frac{\partial \mathbf{M}}{\partial x_j}\right)^2 - M_iH_i - \sigma_{ik}u_{ik}, \tag{6.2}$$

$\varphi(M^2)$ and $\alpha_0(\partial M/\partial x_j)^2$ are the volume energies associated with uniform and nonuniform magnetization, respectively and the term in γ' is the magnetovolume interaction due to the nonuniform magnetization.

In (6.2) we have neglected magnetic interactions and anisotropic magnetostriction, since in Invars the energies associated with these effects are two orders of magnitude smaller than the MVI energy. We have also neglected boundary effects, the effect of the domain structure, and the second-order magnetovolume interaction.

For the effective stress tensor $\tilde{\sigma}_{ik} = \partial\phi/\partial u_{ik}$ and the magnetic field

$$\tilde{\mathcal{H}}_i = -\left[\frac{\partial\phi}{\partial M_i} - \frac{\partial}{\partial x_k}\left(\partial\phi/\partial\frac{\partial M_i}{\partial x_k}\right)\right]$$

we obtain from (6.1)

$$\tilde{\mathcal{H}}_i = H_i - 2\varphi'(M^2)M_i - 2\gamma u_{kk}M_i + (\alpha_0 + \gamma' u_{kk})\frac{\partial^2 M_i}{\partial x_k \partial x_k}, \tag{6.3}$$

$$\tilde{\sigma}_{ik} = c^0_{iklm}u_{lm} + \gamma M^2\delta_{ik} + \frac{1}{2}\gamma'\left(\frac{\partial \mathbf{M}}{\partial x_j}\right)^2\delta_{ik} - \sigma_{ik}.$$

The equations of motion have the form

$$\frac{\partial \mathbf{M}}{\partial t} = \frac{2\mu_B}{\hbar}[\tilde{\mathcal{H}}\mathbf{M}] + \mathbf{R}, \quad \rho\frac{\partial^2 u_i}{\partial t^2} = \frac{\partial\tilde{\sigma}_{ik}}{\partial x_k}, \tag{6.4}$$

where u_i is the displacement vector, ρ is the density, and $\mathbf{R}$ is the relaxation term.

Equilibrium equations of state of the form (3.2) and (5.2) can be obtained from (6.3) by neglecting the spatial derivatives in the equations $\tilde{\mathcal{H}}_i = 0$, $\tilde{\sigma}_{ik} = 0$. Here we will assume

$$\varphi(M^2) = \frac{1}{2}a_0M^2 + \frac{1}{4}b_0M^4,$$

which is correct for an arbitrary ferromagnet near T_c (Ref. 24). Then from (6.3) we obtain the magnetic equation of state (5.3) and the equilibrium deformation $u^0_{ik} = -B_0^{-1}(\gamma M^2 + P)\delta_{ik}/3$. The dependence of the susceptibilities and the magnetization on the external magnetic field H will be needed below. From (5.3) we have

$$M_0(H) \approx M_0(0) + \chi_P H,$$

$$M_0^2(0) = -\frac{a}{b}, \quad \chi_P^{-1}(H) \approx \chi_P^{-1}(0) + 3\frac{H}{M_0},$$

$$\chi_P^{-1}(0) = a + 3bM_0^2 = 2bM_0^2,$$

$$\chi_V^{-1} = \chi_P^{-1}\frac{b_0}{b}, \quad \chi_V^{-1}(H) = \chi_V^{-1}(0) + 3\frac{b_0}{b}\frac{H}{M_0}.$$

Recall that χ_V and χ_P are the longitudinal susceptibilities at constant volume and pressure, respectively, and they depend on pressure.

6.1. Fluctuation corrections to the equations of state

The effect of spin fluctuations on the thermodynamic properties with magnetovolume interactions taken into account was considered in Refs. 9, 32, 33. However the method used to calculate the fluctuation corrections in Ref. 32 is hardly systematic. The contribution of transverse fluctuations of the magnetic moment was not taken into account in Ref. 9. Our approach[31] assumes the Gaussian approximation and the results are similar to the conclusions of Ref. 33. In addition, our approach includes magnetovolume interactions with a nonuniform magnetization, which were not taken into account in Refs. 9, 32, and 33.

A similar problem to that considered here was discussed in Refs. 11 and 25. The effect of magnetovolume interactions on the critical behavior of the ferromagnet was discussed in Ref. 25 using the Heisenberg model. It was found that magnetovolume interactions change the frequencies of spin waves and phonons (see the bibliography given in Ref. 11). The effect of such changes on the thermodynamic properties are not easy to estimate because of the complexity of the analytical expressions and the fact that they involve unknown parameters.

Fluctuations are taken into account in the Gaussian approximation by putting $\mathbf{M} = \mathbf{M}_0 + \mathbf{m}(\mathbf{x})$ and $u_{ik} = u^0_{ik}$ into (6.1) and keeping terms no higher than m^2. We then perform a functional integration with respect to $\mathbf{m}(\mathbf{x})$ in the expression

$$Z = \sum \exp\left(-F\frac{(\mathbf{m}(\mathbf{x}))}{k_BT}\right).$$

Strictly speaking, we should write $u_{ik} = u^0_{ik} + \Delta_{ik}$ and integrate with respect to Δ_{ik} as well, in order to take into account displacement fluctuations (or phonons) in an equivalent way. However, it was shown in Ref. 25 that this added complication does not change the results in our approximation.

Transforming to a Fourier expansion for $m(x)$ and carrying out the calculation, we obtain the following expression for the equilibrium thermodynamic potential $\Psi = (k_BT/V)\ln z$:

$$\Phi(P, T, H) = \Phi_0(P, T, H) - \frac{k_BT}{2V}\sum_{\mathbf{k}}\ln\chi_\nu(\mathbf{k}). \tag{6.5}$$

The subscript ν in (6.5) signifies the contribution of the longitudinal ($\|$) and the two transverse ($\perp$) components of the magnetic moment. Also

$$\langle|m_{\mathbf{k}}^{\nu}|\rangle = \frac{k_B T}{V}\chi_{\nu}(\mathbf{k}), \quad \chi_{\nu}(\mathbf{k}) = (\chi_{\nu}^{-1} + \alpha k^2)^{-1},$$

$$\chi_{\parallel}^{-1} = \chi_V^{-1} + 3\frac{b_0}{b}\frac{H}{M_0},$$

$$\chi_{\perp}^{-1} = H/M_0, \quad \alpha = \alpha_0[1 - \frac{\gamma'}{\alpha_0 B_0}(\gamma M_0^2 + P)], \tag{6.6}$$

$$\Phi_0(P, T, H) = \frac{1}{2}aM_0^2 + \frac{1}{4}bM_0^4 - \frac{P^2}{2B_0} - HM_0, \tag{6.7}$$

$\Psi_0(P,T,H)$ is the equilibrium thermodynamic potential in the mean-field approximation.

The constant α in (6.6) is renormalized by the volume-elastic interaction and depends on pressure. By comparing with the experimental $D(P)$ dependence for Fe–Ni alloys,[34] it follows that $\gamma' \approx -\gamma a^2$ (a is the lattice constant), where $D = 2\mu M\alpha/\hbar$. The potential (6.7) leads to the same results as (5.2).

The equations of state with fluctuation corrections are obtained from (6.5) using the relations $\omega = \partial\Phi/\partial P$ and $M = -\partial\Phi/\partial H$:

$$M = M_0 - \frac{1}{2M_0}(3\frac{b_0}{b}\langle m_{\parallel}^2\rangle + 2\langle m_{\perp}^2\rangle), \tag{6.8}$$

$$\omega = \omega_0 + \frac{2\gamma}{B_H}\langle m_{\parallel}^2\rangle - \frac{\gamma'}{2B_H}\sum_{\mathbf{k}}[\langle|m_{\mathbf{k}}^{\parallel}|^2\rangle + 2\langle|m_{\mathbf{k}}^{\perp}|^2\rangle]k^2,$$

$$T < T_c, \tag{6.9}$$

$$\omega = -\frac{P}{B_0} - \frac{\gamma'}{B_0}\langle \mathbf{m}^2\rangle - \frac{\gamma'}{2B_0}\sum_{\mathbf{k}}\langle|\mathbf{m}_{\mathbf{k}}|^2\rangle k^2, \quad T > T_c; \tag{6.10}$$

where $\langle m_{\parallel,\perp}^2\rangle = \Sigma_k\langle|m_k^{\parallel,\perp}|^2\rangle$. In the derivation of (6.9) and (6.10) we used the relations $\partial\chi_{\parallel}^{-1}/\partial P = 4\gamma/B_H$, $\partial\alpha/\partial P = -\gamma'/B_H$ for $T < T_c$ and $\partial\chi^{-1}/\partial P = -2\gamma/B_0$, $\partial\alpha/\partial P = -\gamma'/B_0$ for $T > T_c$.

The magnetization formula (6.8) reduces to the expression of Ref. 29 when $\langle m_{\parallel,\perp}^2\rangle/M_0^2 \ll 1$, except for the factor b_0/b in front of $\langle m_{\parallel}^2\rangle$. Since $b_0/b > 1$, it is evident from (6.8) that the magnetovolume interaction amplifies the contribution of longitudinal fluctuations to the temperature dependence of the magnetization.

It follows from (6.9) ($\gamma < 0$) that the contribution of fluctuations to the volume deformation is negative, while the spontaneous volume magnetostriction $\omega_0(P=0)$ is positive. Qualitatively the same result was obtained in Ref. 32, but there the fluctuation contribution was $\sim\gamma^{-1}$, while in (6.9) it is proportional to γ, which seems more likely. Our conclusion about the sign of the fluctuation contribution to ω contradicts the results of Refs. 9 and 33 below T_c but agrees with them for $T > T_c$. The signs of the fluctuation contribution to ω in (6.9) and (6.10) are different because the coefficient a changes sign when the temperature passes through T_c. The result is a negative contribution to the thermal expansion both above and below T_c, which is a consequence of the fact that $\langle m_{\parallel}^2\rangle$ increases with increasing temperature below T_c and $\langle \mathbf{m}^2\rangle$ decreases with increasing temperature above T_c. This behavior of $\langle m_{\parallel}^2\rangle$ and $\langle \mathbf{m}^2\rangle$ follows from (6.6) when only long-wavelength thermal fluctuations of the magnetic moment are taken into account.

Using (6.10), we can estimate the fluctuation contribution to the coefficient of linear expansion β and the bulk modulus for $T > T_c$. Using the fact that $B^{-1} = -\partial\omega/\partial P$ and neglecting the pressure dependence of α in (6.10) and also the last term, we obtain

$$\frac{\Delta B}{B} = \frac{B - B_0}{B} = -\frac{3\gamma^2 k_B T\chi^{1/2}}{8\pi B_0\alpha^{3/2}}. \tag{6.11}$$

As already noted, these approximations correspond to taking into account only long-wavelength critical fluctuations in $\langle \mathbf{m}^2\rangle$ with the help of (6.6). With the same approximations we have for $\Delta\beta = (1/3)\partial\omega/\partial T$

$$\Delta\beta = \frac{\gamma}{B_0}\frac{3k_B T\chi^{1/2}}{16\pi\alpha^{3/2}}\frac{\partial\chi^{-1}}{\partial T}. \tag{6.12}$$

We note that expressions analogous to (6.11) and (6.12) for the fluctuation contribution to the heat capacity ΔC_P were discussed in Ref. 24. Also, (6.12) is consistent with (5.9), i.e. in (6.12) $\Delta\beta \sim \Delta C_P$. Using the following values of the physical parameters for $Fe_{65}Ni_{35}$ from Ref. 16: $\gamma = -1.6\cdot 10^4$ G^{2}cm^3/erg, $B_0 \approx 2\cdot 10^{12}$ erg/cm^3, $\alpha \approx 10^{-12}$ G^{2}cm^5/erg, $\chi \approx 4\cdot 10^{-4}$ erg/cm^{3}G^2, $T = 5.5\cdot 10^2$ °K $> T_c$; $\partial\chi^{-1}/\partial T \equiv C^{-1} \approx 6$ G^{2}cm^3/erg·deg, we find that $\Delta B/B \simeq -2\cdot 10^{-2}$ and $\Delta\beta \simeq -3\cdot 10^{-6}$ °K^{-1}, which agree in order of magnitude and in sign with the experimental data.[1]

A positive magnetic contribution to β above T_c was predicted in Ref. 9. According to Ref. 9, $\langle m^2\rangle$ increases when $T > T_c$. This is a result of the fact that the long-wavelength critical fluctuations of the magnetization were not taken into account correctly in calculating $\langle m^2\rangle$. To be fair it must be said that the conclusions of Ref. 9 are correct for many collective magnetic materials outside the region where critical fluctuations of the magnetization are strong.

In connection with the derivation of (6.8), it is known from the spin-wave approximation that the temperature dependence of the magnetization

$$\langle s_z\rangle = s - \langle b^+ b\rangle$$

can be rewritten in the form

$$M = M_0 - \frac{\langle m_{\perp}^2\rangle}{M_0},$$

where $M_0 = g\mu ns$, $M = g\mu n\langle s_z\rangle$, $\langle m_{\perp}^2\rangle = (g\mu n)^2\langle s_x^2\rangle$, $\langle s_x^2\rangle = s\langle b^+ b\rangle$; $b+$ and b are the spin deviation operators. We can consider (6.8) to be a generalization of the above formula to the case when longitudinal fluctuations of the magnetic moment are taken into account.

For Invars there is the problem of "hidden" magnetic excitations.[35] The coefficient D in the dispersion equation for spin waves $\omega = Dk^2$ has one value when determined from magnetic measurements, and a different value when obtained from neutron-diffraction experiments, i.e. spin waves do not explain the temperature dependence of the magnetization in Invars even at low temperatures. Therefore (6.8) suggests that there are "hidden" magnetic excitations in Invars among the longitudinal fluctuations of the magnetic moment. The hidden excitations could be longitudinal excitations of the paramagnetic type[29] or longitudinal spin fluctuations ("diffusions").[36]

We recall that in the theory of spin-phonon interac-

tions, when the anharmonicity of the lattice vibrations is taken into account, an additional term $\sim T^4$ appears in the temperature dependence of the magnetization;[10a,b] see also (5.4)–(5.6) above. This term is comparable to the contribution of the spin-spin interaction to the temperature dependence,[10] and obviously cannot explain the dependence $M(T)$ in Invars.

6.2. Propagation of sound waves with magnetovolume interactions

6.2.1. Dispersion of the speed of sound

For small deviations from equilibrium we have from (6.3)

$$\tilde{\mathscr{H}}_i = -\chi_{ij}^{-1} m_j + \alpha \nabla^2 m_i - 2\gamma M_{0i} \Delta_{kk} + \gamma' \Delta_{kk} \nabla^2 m_i,$$

$$\tilde{\sigma}_{ik} = c^0_{iklm} \Delta_{lm} + 2\gamma M_{0l} m_l \delta_{ik}; \qquad (6.13)$$

here $\Delta_{ik} = (1/2)(\partial u_i/\partial x_k + \partial u_k/\partial x_i)$, $\chi_{ij}^{-1} = 4M_{0i} M_{0j} \varphi''(M_0^2) + [2\varphi'(M_0^2) + 2\gamma u_{ll}^0]\delta_{ij}$ is the reciprocal of the susceptibility for $u_{ij} = \text{const}$.

It is evident from (6.13) that in the linear approximation only the component of $\mathbf{m}$ parallel to $\mathbf{M}_0$ (m_z if $\mathbf{M}_0$ is along z) interacts with sound waves. In this approximation $m_z \equiv m$ participates in the relaxation and diffusion motions.

We take $R_i = \mathscr{H}_i/\tau_1$ for the relaxation term. Then we obtain for sound waves interacting with the magnetic subsystem[37]

$$\rho \frac{\partial^2 u_i}{\partial t^2} = c^0_{iklm} \frac{\partial^2 u_l}{\partial x_k \partial x_m} + 2\gamma M_0 \frac{\partial m}{\partial x_i},$$

$$\frac{\partial m}{\partial t} = -\frac{m}{\tau_1 \chi_\parallel} - \frac{M_0}{\tau_1} \Delta_{zz}. \qquad (6.14)$$

We have put $\chi_{zz} \equiv \chi_\parallel$ and have neglected the term involving the spatial derivatives of m in the second equation of (6.14).

As an example, we consider the propagation of sound in the [110] direction in a cubic crystal.

For sound waves propagating and polarized in the x,y plane, we substitute in (6.14) a solution of the form $u_{ij} m \sim \exp[i\{[k/\sqrt{2}(x+y)] - \omega t\}]$. From the condition for a nontrivial solution for u_i and m we obtain the dispersion relation

$$(\omega^2 - c_{0T}^2 k^2)\left[(\omega^2 - c_{0L}^2 k^2)\left(-i\omega + \frac{1}{\tau_1 \chi_\parallel}\right) - \frac{4\gamma^2 M_0^2}{\tau_1} k^2\right] = 0, \qquad (6.15)$$

where

$$\rho c_{0T}^2 = \frac{1}{2}(c^0_{11} - c^0_{12}), \quad \rho c_{0L}^2 = \frac{1}{2}(c^0_{11} + c^0_{12} + 2c^0_{44}).$$

We conclude that magnetovolume interactions do not affect the propagation of transverse sound. This conclusion is correct if we neglect the second-order magnetovolume interaction. If the second-order interaction is included the following substitutions must be made in (6.15):

$$c^0_{ik} \to c^0_{ik} + \varepsilon_{ik} M^2 \equiv c^M_{ik}, \quad \gamma \to \gamma[1 - (\varepsilon_{11} + 2\varepsilon_{12}) M_0^2 (3B_M)^{-1}].$$

But even in this case transverse sound waves do not experience dispersion or attenuation, which is in agreement with experiment.[40]

For longitudinal sound waves

$$c^2(\omega) = \frac{\omega^2}{k^2} = (1 - i\omega\tau)^{-1}(c_L^2 - i\omega\tau c_{0L}^2); \qquad (6.16)$$

$c_L^2 = c_{0L}^2 - 4\gamma^2 M_0^2 \chi_\parallel/\rho$ is the square of the equilibrium speed of sound and $\tau = \tau_1 \chi_\parallel$ is the relaxation time of the longitudinal component of the magnetization. The result (6.16) is identical to the Mandel'shtam–Leontovich result.[38] It follows from (6.16) that when $\omega\tau \gg 1$ we have $c = c_{0L}$ and when $\omega\tau \ll 1$ we have $c = c_L$. The attenuation is small, i.e. $\text{Im}\, k/|k| \ll 1$, in the high-frequency and low-frequency limits.

Propagation of longitudinal sound causes a variation in the volume, which then leads to a variation in the magnetization because of magnetostriction. When $\tau \gg \omega^{-1}$ the magnetization cannot reach the equilibrium value and the speed of sound is determined by the elastic constants with $M = \text{const}$. When $\tau \ll \omega^{-1}$ the magnetization can reach the equilibrium value and the speed of sound is determined by the equilibrium elastic constants. It is not difficult to see from (6.16) and (3.8) that they are equal to c_{ik}^H.

All these conclusions are supported experimentally, as is evident from Fig. 2. The temperature dependence of the quantity $(c_{11} + c_{12} + 2c_{44})/2$ is shown for the alloy $Fe_{65}Ni_{35}$ as determined by neutron diffraction,[39] along with the measurements of the speed of ultrasound.[14,40,41] Neutrons measure the speed of sound with frequency $\omega \gtrsim 10^{12}$ sec^{-1}, while the frequency of ultrasound is $\sim 10^7$ Hz. We see from Fig. 2 that the elastic constants determined from high-frequency and low-frequency measurements differ by about 27%, which is consistent with the estimate $\rho(c_{0z}^2 - c_z^2) = 4\gamma^2 M^2 \chi_\parallel \approx 0.6 \cdot 10^{11}$ N/m^2. We have considered this example in detail because it illustrates an important fact concerning the different times associated with first and second-order magnetovolume interactions. The interaction time associated with the first-order magnetovolume interaction is determined by the relaxation time of the magnetization and $\tau \sim 10^{-10}$ sec. The time scale associated with the second-order magnetovolume interaction is evidently $\lesssim 10^{-13}$ sec. We see from Fig. 2 that the difference between the high-frequency and low-frequency speeds of sound persists above T_c, where the Mandel'shtam—Leontovich

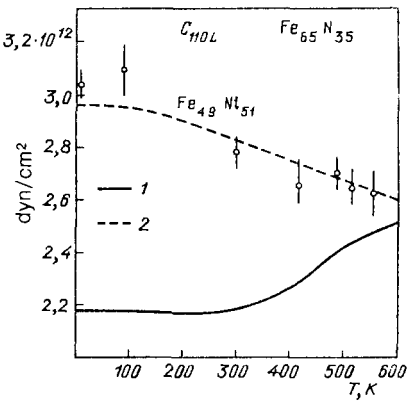

FIG. 2. Temperature dependence of the elastic modulus $(c_{11} + c_{12} + c_{44})/2$ in $Fe_{65}Ni_{35}$ (neutrons). Curves: results obtained from the measured speed of sound in $Fe_{65}Ni_{35}$ (1) and $Fe_{49}Ni_{51}$ (2) (Ref. 37).

mechanism does not operate. The dispersion of the speed of sound above T_c can be explained in terms of interactions between volume deformations and magnetization fluctuations.[42] The effect of magnetovolume interactions on the lattice is not limited to small k. Anomalies in the dispersion curves of transverse phonons measured in the (110) direction were observed in Ref. 43 in Fe_3Pt and $Fe_{65}Ni_{35}$ for $k \simeq 0.5\pi/a$. A maximum in the dependence of the width of phonon resonances on k lies in this wavevector region. It was concluded in Ref. 43 that the electron-phonon interaction is amplified when the wavevector is equal to half the size of the Brillouin zone. These facts have yet to be explained.

6.2.2. Effective anharmonicity of the elastic subsystem

The elastic part of the thermodynamic potential of a solid has the form

$$\Phi = \frac{1}{2} c^{(2)} \hat{u}\hat{u} + \frac{1}{6} c^{(3)} \hat{u}\hat{u}\hat{u}$$

to third order in the deformation tensor $\hat{u}$. Here $c^{(2)} \sim 10^{11}$ N/m^2 are the second-order elastic constants, which have already been considered, and $c^{(3)} \sim 10^{12}$–10^{13} N/m^2 are the third-order elastic constants and correspond to nonlinear acoustic effects.

In magnetic materials the elastic subsystem interacts with the magnetic subsystem and this interaction leads to corrections $\Delta c^{(2)}$ and $\Delta c^{(3)}$. As noted above, for Invars $\Delta c^{(2)}/c^{(2)}$ reaches several dozen percent, which is of the same order as in antiferromagnetic hematite. The effective anharmonicity of the elastic subsystem of an antiferromagnet was considered in Ref. 44 and it was shown that it should exceed the intrinsic anharmonicity by a factor of 30–100. This conclusion has been supported experimentally.[45] We calculate the second-order elastic constants and the effective third-order elastic constants $\Delta c^{(3)}$ for Invars following Ref. 16. We analyze the symmetry of the elastic constants and estimate their magnitudes.

Starting from the thermodynamic potential in the form (3.1), we write down the following equations for the longitudinal component of the effective field $\tilde{\mathscr{H}} \equiv \tilde{\mathscr{H}}_z$ and the effective stress tensor $\tilde{\sigma}_{ik}$ to within quadratic terms in $m \equiv m_z$ and Δ_{ik}:

$$\begin{aligned}\tilde{\mathscr{H}} &= -\chi_\parallel^{-1} m - [\tfrac{3}{2}(\chi_\parallel^{-1} M_0^{-1} - H M_0^{-2}) \\ &\quad + 4M_0^3 \varphi'''(M_0^2)]m^2 - 2\Gamma_{ik}\Delta_{ik} m \\ &\quad - 2M_0 \Gamma_{ik}\Delta_{ik} - M_0 \varepsilon_{iklm}\Delta_{ik}\Delta_{lm}, \\ \tilde{\sigma}_{ik} &= (c^0_{iklm} + \varepsilon_{iklm} M_0^2)\Delta_{lm} + 2M_0 \Gamma_{ik} m \\ &\quad + \Gamma_{ik} m^2 + 2M_0 \varepsilon_{iklm}\Delta_{lm} m.\end{aligned}$$

$\chi_\parallel$ is the longitudinal susceptibility with $u_{ik} = \text{const}$ ($\chi_\parallel \equiv \chi_T$).

Solving the equation $\tilde{\mathscr{H}} = 0$ for m up to quadratic terms in Δ_{ik} and substituting the result into $\tilde{\sigma}_{ik}$, we obtain

$$\tilde{\sigma}_{ik} = c^{(2)}_{iklm}\Delta_{lm} + \frac{1}{2} c^{(3)}_{iklmrs}\Delta_{lm}\Delta_{rs},$$

where

$$c^{(2)}_{iklm} = c^0_{iklm} + \varepsilon_{iklm} M_0^2 - 4M_0^2 \chi_\parallel \Gamma_{ik}\Gamma_{lm}, \tag{6.17}$$

$$\begin{aligned}\Delta c^{(3)} \equiv c^{(3)}_{iklmrs} &= 8(3M_0 H - 8M_0^6 \varphi'''(M_0^2))\chi_\parallel^3 \Gamma_{ik}\Gamma_{lm}\Gamma_{rs} \\ &\quad - 4\chi_\parallel M_0^2 \Gamma_{ik}\varepsilon_{lmrs} - 8M_0^2 \chi_\parallel \varepsilon_{iklm}\Gamma_{rs}.\end{aligned} \tag{6.18}$$

These equations hold for $\omega\tau \ll 1$, since the equation $\tilde{\mathscr{H}} = 0$ is the equilibrium condition. Therefore $c^{(2)}_{iklm} \equiv c^H_{iklm}$, which can be seen from (3.8).

In a cubic crystal there are six independent third-order elastic constants. However in the effective elastic tensor in (6.18) not all the components are of the same order of magnitude. Converting to the three-index notation for $c^{(3)}_{iklmrs}$ following Ref. 46, we find

$$\begin{aligned}c^{(3)}_{111} &\simeq 8(3M_0 H - 8M_0^6 \varphi'''(M_0^2))\chi_\parallel^3 \gamma^3 - 12M_0^2 \chi_\parallel \gamma \varepsilon_{11}, \\ c^{(3)}_{112} &\simeq 8(3M_0 H - 8M_0^6 \varphi'''(M_0^2))\chi_\parallel^3 \gamma^3 \\ &\quad - 8M_0^2 \chi_\parallel \gamma \varepsilon_{11} - 4M_0^2 \gamma \chi_\parallel \varepsilon_{12}, \\ c^{(3)}_{123} &\simeq 8(3M_0 H - 8M_0^6 \varphi'''(M_0^2))\chi_\parallel^3 \gamma^3, \quad c^{(3)}_{456} \approx 0.\end{aligned} \tag{6.19}$$

The other nonzero components of the tensor $c^{(3)}$ reduce to the terms written out in (6.19).

Numerical estimates based on (6.19) for the alloys $Fe_{65}Ni_{35}$ and Fe_3Pt show that the first three elastic constants in (6.19) are larger than the last constant. Therefore nonlinear elastic effects in Invars should be observed mainly for longitudinal sound waves. The largest constants are $c^{(3)}_{111}$ and $c^{(3)}_{123}$. They should increase with increasing temperature and reach the value 10^{13} N/m^2 near T_c, which is several times larger than the intrinsic anharmonicity.

Finally, we discuss a possible experiment to observe nonlinear acoustic effects in Invars.

For a longitudinal sound wave of fixed frequency propagating in the (100) direction in a cubic crystal, at a distance r from the boundary of the sample a wave of twice the frequency of the incident sound wave should be observable with the amplitude

$$u'' = \frac{c^{(3)}_{111}}{c^2} \frac{k^2 u_0^2}{8} r;$$

here u_0, $c = (c_{11}/\rho)^{1/2}$, and k are the amplitude, propagation velocity, and wave number of the first harmonic, respectively. Attenuation of the wave was not taken into account. A similar calculation was given in Ref. 47. It follows that nonlinear effects in Invars should be observable for attainable values of the deformation $u_0 \sim 10^{-6}$ in the primary wave.

6.3. Dynamics of the spin system

6.3.1. Attenuation of spin waves

Experimental data[48] indicate strong attenuation of spin waves in Invars, and $\text{Im}\,\omega(k) \equiv \Gamma(k,T) = \Gamma_0 k^2$ in the pseudomomentum interval $k \sim (0.01$–$0.3)\pi/a$, where $\Gamma_0/D \simeq 0.05$, $\text{Re}\,\omega(k) = Dk^2$. As mentioned in Ref. 48, these results cannot be explained by the magnon-magnon interaction $\Gamma(k,T) \sim T^2 k^4$ or by the electron-phonon interaction with $\Gamma(k,T) \sim T^2 k^3$ and the attenuation is obviously not connected with magnetic inhomogeneities of Fe–Ni Invar, because the same effect is observed in the homogeneous ordered alloy $Fe_{72}Pt_{28}$. Therefore the source of the strong attenuation of magnons in Invars is not clear.

We consider the effect of magnetovolume interactions on the propagation of spin waves. From (6.4) and (6.11) we

obtain an equation of motion for the transverse component of the magnetization vector

$$ih\dot{m}^+ = 2\mu M_0\alpha\nabla^2 m^+ + 2\mu M_0\gamma' \frac{\partial u_l}{\partial x_l}\nabla^2 m^+ - 2\mu M_0\gamma \frac{\partial u_l}{\partial x_l} m^+, \tag{6.20}$$

where $m^+ = m_x + im_y$. It follows that linear magnetoacoustic resonance at the intersection of the dispersion branches of acoustic and spin waves does not occur. The condition for resonance is a linear term in $\partial u/\partial x$ in the equation for spin waves, while (6.20) contains MVI terms in the combination $m(\partial u/\partial x)$. It also follows from (6.20) that spin waves interact only with longitudinal sound waves.

To solve (6.20), we apply a method similar to that used in Ref. 49. Taking the Fourier transform of (6.20) and averaging, we obtain

$$(\omega - Dk^2)\langle m^+(\mathbf{k},\omega)\rangle + \frac{iA}{(2\pi)^4} \times \int k'^2(k_l - k'_l)\langle u_l(\mathbf{k}-\mathbf{k}', \omega-\omega')m^+(\mathbf{k}',\omega')\rangle d\mathbf{k}'d\omega' = 0.$$

We have introduced the notation $\hbar D = 2\mu M_0\alpha$, $\hbar A = 2\mu M_0\gamma'$ and we have neglected the last term in (6.20).

Decomposing the correlation function inside the integral, we have the following equation for the modified dispersion equation for spin waves to lowest order in A

$$(\omega - Dk^2)\langle m^+(\mathbf{k},\omega)\rangle + \frac{A^2}{(2\pi)^8}\int \frac{(k_l - k'_l)(k'_m - k''_m)k'^2 k''^2}{(\omega' - Dk'^2)} \times\langle u_l(\mathbf{k}-\mathbf{k}', \omega-\omega')u_m(\mathbf{k}'-\mathbf{k}'', \omega'-\omega'')\rangle \times\langle m^+(\mathbf{k}'',\omega'')\rangle d\mathbf{k}'d\omega' d\mathbf{k}''d\omega'' = 0.$$

As shown in Ref. 31, this equation gives the following expression for $\mathrm{Im}\,\omega(k) = \Gamma(k)$:

$$\Gamma(k) = \Gamma_0 k^2 = \frac{3k_B T A^2}{16\pi Mc^2 D}\frac{k_x^3}{k_D^3}k^2, \tag{6.21}$$

where $k_x = c/D$, k_D is the Debye wave number, and M is the mass of the atom.

The result (6.21) is correct in the limit $k\to 0$ and at finite temperatures. It is consistent with the results of Refs. 10 and 50, which were obtained by considering the spin-phonon interaction in the Heisenberg model, and represents the attenuation of magnons because of inelastic scattering by phonons.

To estimate the magnitude of the attenuation in Invars we use $\hbar D = 2.4\cdot 10^{-40}$ J·m^2, $c = 5\cdot 10^3$ m/sec, $k_D \approx \pi/a$, $\gamma' \approx -\gamma a^2$, $T = 300$ °K. Then with the help of (6.21) we obtain $\Gamma_0/D \approx 0.002$, which is only about 5% of the experimental value.

Apparently a solution of this problem can be obtained only outside the scope of perturbation theory. In this connection see also Ref. 51.

6.3.2. Parametric amplification of spin waves

Here we consider the excitation of spin waves in Invar by an external pumping sound wave. The possibility of this effect follows from (6.20). We consider the steady case, when a longitudinal sound wave with frequency ω transfers energy to two spin waves with frequencies ω_1 and ω_2 propagating in the same direction. The frequencies and wave numbers of the pumping wave and the amplified waves are related by the conditions

$$\omega = \omega_1 + \omega_2, \quad k = k_1 + k_2, \tag{6.22}$$

which can be interpreted as the laws of conservation of energy and momentum for the elementary process in which a quasiparticle corresponding to the pumping wave is annihilated and two quasiparticles corresponding to the generated spin waves are created.

In (6.20) we introduce terms taking into account the effect of an external magnetic field and the attenuation of spin waves $\sim\beta\dot{m}^+$. Then in the case of plane waves propagating along the z axis, (6.20) takes the form

$$i\dot{m}^+ + \omega_H m^+ - D\frac{\partial^2 m^+}{\partial z^2} + \beta\dot{m}^+ = A\frac{\partial u_z}{\partial z}\frac{\partial^2 m^+}{\partial z^2} + 2\frac{A}{a^2}\frac{\partial u_z}{\partial z}m^+; \tag{6.23}$$

where $\omega_H = 2\mu H/\hbar$. The longitudinal pumping sound wave is assumed to be undamped: $u_z = u\exp[i(\omega t - kz)] + \text{c.c.}$, where u is a given constant, ω and $k = \omega/c$ are the frequency and wave number of the elastic wave. A consequence of parametric resonance is the generation of two spin waves by a sound wave propagating along the z axis. When the amplitude of the sound wave u exceeds a threshold value u_{th}, the amplitudes of the spin waves will increase according to the equation $m_{1,2}(z) = m_{1,2}^0\exp(\theta z)$, where θ is the growth constant. The threshold amplitude is obtained from (6.23) following the procedure described in Refs. 31 and 52:

$$u_{\text{th}} = \frac{(\Gamma_1\Gamma_2)^{1/2}a^2}{kA^2[(2+k_1^2a^2)(2+k_2^2a^2)]}.$$

To obtain a quantitative estimate of $u_{\text{th}0}$ we take $\Gamma_1 \approx \Gamma_2 \approx \Gamma$; $\Gamma_{1,2} = \Gamma_0 k_{1,2}^2$, $k_1 \sim k_2 \sim k/2$, $\omega = ck$, $\omega \approx 10^{11}$ sec^{-1}, and we use the physical parameters of Fe–Ni Invar given above. Then we obtain $u_{\text{th}} \sim 10^{-13}$ m, which corresponds to an elastic wave intensity of a hundreth of a watt through a cross-sectional area of ~ 10 mm^2. In spite of the strong attenuation of spin waves in Invars, the threshold amplitude is not large because of the large value of the MVI constant.

The growth constant is $\theta = (\Gamma/Dk)(\zeta - 1)$, where $\zeta = |u|/u_{\text{th}}$. When the threshold power is exceeded by 1% the factor $(\zeta - 1) \approx 0.005$ and at a frequency of $\omega \sim 10^{11}$ sec^{-1} we have $\theta \simeq 50$. Hence the spin wave power increases by a factor of 10^{30} over a distance of 1 cm, which is obviously impossible and so there must be an effective limitation on the power of the elastic wave that can be transferred to the spin waves.

The conditions of parametric resonance for the wave-vectors and frequencies of the waves being amplified can be obtained from (6.22) and the dispersion relations $\omega_{1,2} = \omega_H + Dk_{1,2}^2$. In an experimental test of these results it is simplest to observe saturation in the power of the elastic (hypersonic) pumping wave leaving the crystal. The existence of spin waves exceeding the thermal level can be observed in neutron diffraction experiments. However, because of experimental difficulties connected with the finite angular and energy resolutions of present-day neutron spec-

trometers, the frequency of the pumping sound wave must exceed 10^{12} sec^{-1}. Hence parametric amplification of spin waves by sound may be another method of studying magnetovolume interactions in Invars.

6.4. Coupling between magnetization and displacement fluctuations and diffraction effects

It is natural to expect that, in addition to the magnetoelastic coupling between the magnetization and uniform volume deformations, the fluctuations of these quantities should also be coupled. Magnetization fluctuations usually increase strongly near the Curie point. In some ferromagnets, including Fe–Ni Invar, magnetization fluctuations caused by fluctuations in composition are also observed at low temperatures.[53,54] Because of the magnetovolume interaction these fluctuations cause displacements of atoms, which can be observed as a weakening of the intensity of Bragg reflections and an increase in diffuse scattering of radiation incident on the crystal. Following Ref. 55, we obtain the correlation function of the atomic displacements caused by the magnetovolume interaction.

An expression for the displacement vector caused by small deviations of the magnetization m_i from the equilibrium value M_0 is determined by requiring the body forces to vanish: $\partial\tilde{\sigma}_{ik}/\partial x_k = 0$. A similar method has been used to analyze the distortions in a solid solution due to fluctuations in the composition[56] and to calculate the diffuse scattering by displacements caused by precipitations of the new phase.[57] We use (6.13) plus the additional term m^2 for $\tilde{\sigma}_{ik}$. Then we have for the Fourier component of the displacement vector

$$u_i(\mathbf{q}) = 2i\gamma M_{ij}^{-1}[M_0 m_l + \sum_{\mathbf{k}} m_l(\mathbf{q}-\mathbf{k})m_l(\mathbf{k})]q_j,$$

where M_{ij}^{-1} is the matrix inverse of M_{ij}. For cubic crystals

$$M_{ij} = (c_{12}+c_{44})q_iq_j + [c_{44}q^2 + (c_{11}-c_{12}-2c_{44})q_i^2]\delta_{ij}.$$

We then obtain the following expression for the Fourier transform of the displacement correlation function:

$$\langle u_i u_j^* \rangle = \frac{k_BT}{V}\frac{4\gamma^2}{c_{11}^2q^4}\left[\frac{M_0^2}{\chi_\parallel^{-1}+\alpha q^2} + \frac{k_BT}{8\pi\alpha^2 q}\left(\operatorname{arctg}\frac{qr_{c\parallel}}{2} + 2\operatorname{arctg}\frac{qr_{c\perp}}{2}\right)\right]q_iq_j, \qquad (6.24)$$

$r_{c\parallel,\perp} = (\chi_{\parallel,\perp}\alpha)^{1/2}$ are the correlation lengths. This expression is valid for $T \lesssim T_c$ for an elastically isotropic solid. The first term within the braces is the contribution of second-order magnetization fluctuations and the second term is the contribution of fourth-order magnetization fluctuations. When $T > T_c$ the displacement correlation function can be found from (6.4) by putting $M_0 = 0$ and $r_{c\parallel} = r_{c\perp}$.

The differential cross section for diffuse scattering of neutrons by displacement fluctuations follows from the well-known expression[56]

$$\frac{d\sigma}{d\Omega} = N^2b^2\langle u_i u_j^*\rangle q_{1i}q_{1j}; \qquad (6.25)$$

$\mathbf{q}_1 = \mathbf{Q} + \mathbf{q}$ ($\mathbf{Q}$ is the reciprocal lattice vector), b is the amplitude of neutron scattering by nuclei, and N is the number of atoms in the crystal. The intensity of x-ray scattering can be obtained from (6.25) by replacing b by the atomic form factor for x-ray scattering.

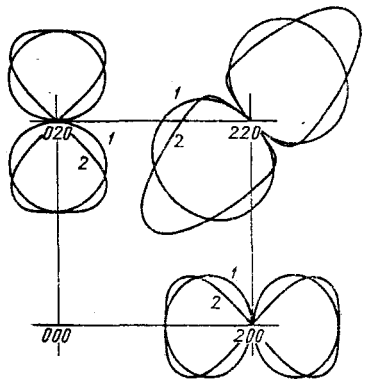

FIG. 3. Polar intensity plots for scattering by atomic displacements in the (001) plane of the reciprocal lattice in the case of volume magnetostriction for $T \lesssim T_c$: *1*) elastically isotropic solid, *2*) cubic crystal $Fe_{65}Ni_{35}$.

Figure 3, taken from Ref. 55, shows polar plots of the intensity around reciprocal lattice points in the (001) plane. The distance between a point on a curve in Fig. 3 and the nearest reciprocal lattice point is a measure of the scattered intensity.

The scattered intensity is maximum along $\mathbf{Q}$ because $\mathbf{u}(\mathbf{q}) \| \mathbf{q}$ in the fluctuation wave. According to (6.25) and (6.24), $d\sigma/d\Omega \propto b$ for Fe–Ni Invar near the lattice point (220). This effect was probably observed in Ref. 58 in diffuse neutron scattering in an $Fe_{68}Ni_{32}$ single crystal. The measured distribution of elastically scattered neutrons and their intensity and temperature dependence correspond closely to the results following from (6.24) and (6.25).

We note that (6.24) and (6.25) predict a sharp decrease (stronger than q^{-2}) in the intensity as we move away from a reciprocal lattice point associated with the fact that the displacement correlation function falls off slowly with distance in real space. The correlation function corresponding to the first term in (6.24) has the form

$$G(r) = \frac{k_BT\gamma^2\chi_\parallel M_0^2}{\pi c_{11}^2}\frac{1}{r}[1-\exp(-\varkappa r)], \quad \varkappa = r_c^{-1},$$

and so the displacement correlations decrease as $1/r$, in contrast to the exponential decay of the magnetic correlations for $T \neq T_c$.

The decrease in the intensity of Bragg reflections is determined by the quantity $\langle u^2\rangle = \Sigma\langle u^2(\mathbf{q})\rangle$, where the summation over $\mathbf{q}$ includes all vectors lying within the first Brillouin zone $0 \leqslant q \leqslant 2\pi/a$. An approximate expression for $\langle u^2\rangle$ valid when $q \ll \pi/a$ can be obtained by replacing the summation over q by an integration from 0 to q_m, where q_m is an adjustable parameter. In (6.21) $q_m \equiv k_D$. Using (6.24) we obtain

$$\langle u^2\rangle = \frac{2\gamma^2M_0^2k_BT}{\pi^2c_{11}^2\alpha}r_c\operatorname{arctg}q_mr_c + \frac{(k_BT)^2\gamma^2}{4\pi^3\alpha^2c_{11}^2} = \begin{cases} \dfrac{q_mr_c}{2}, & \dfrac{q_mr_c}{2} < 1, \\ \dfrac{\pi}{2}\ln\dfrac{q_mr_c}{2}, & \dfrac{q_mr_c}{2} > 1. \end{cases} \qquad (6.26)$$

For Fe–Ni and Fe–Pt Invars, (6.26) gives $\langle u^2\rangle^{1/2} \sim 0.05 \cdot 10^{-8}$ cm at $T \sim 0.95 T_c$. Particularly large values of the scattering cross section (6.25) and the mean-square deviations (6.26) can be expected in magnetic materials with strong magnetovolume interactions and first-order phase transitions. On the spinodal of the magnetic phase $M_0 \neq 0$, $\chi_\parallel \to \infty$, whereas at the Curie point $\chi_\parallel \to \infty$, $M_0 \to 0$. Strong magnetovolume effects, which could possibly be explained with the help of (6.26), were observed experimentally in Ref. 59, in which the anomalous temperature dependence of the intensity of structural reflections was observed in MnAs.

In addition to diffraction effects, displacement fluctuations can cause anomalies in the kinetic properties and can affect the intensity of the Mössbauer spectrum.

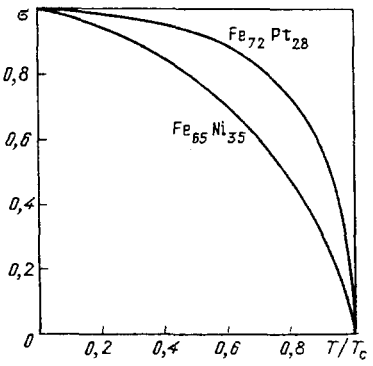

FIG. 5. Temperature dependence of the reduced magnetization of the disordered alloys $Fe_{65}Ni_{35}$ and $Fe_{72}Pt_{28}$ (Ref. 20).

7. DISCUSSION OF THE RESULTS OF THE PHENOMENOLOGICAL THEORY OF MAGNETOVOLUME INTERACTIONS AND COMPARISON WITH EXPERIMENT

We have already given numerical estimates of MVI effects in Invar ferromagnetic alloys. In this Section we compare the results with experiment in more detail. We have chosen the alloys $Fe_{72}Pt_{28}$ and $Fe_{65}Ni_{35}$ because they have been studied extensively experimentally and also because the temperature dependence of the thermodynamic quantities of these alloys is different. In $Fe_{72}Pt_{28}$ the anomalies in the bulk modulus, coefficient of thermal expansion, and $\partial\omega/\partial H$ are concentrated mainly near T_c, whereas in $Fe_{65}Ni_{35}$ the largest anomalies in B and α occur far below T_c. These differences make it possible to consider the role of magnetic inhomogeneities in the Invar problem.

The basic magnetic, thermal, and elastic properties typical of Invar alloys are shown in Figs. 4–10. The difference between the thermodynamic quantities obtained by extrapolation from the paramagnetic state and the experimental values in Figs. 6–10 represent the typical magnetic contribution to the elastic constants and the coefficient of linear expansion of Invar alloys. In addition, the following values are typical for Invar alloys: $\omega \sim 10^{-2}$, $\partial\omega/\partial H \sim 10^9$ Oe^{-1}, $\partial T_c/\partial P \sim$ (3–5) °K/kbar.

It follows from (3.5), (3.8), (3.10), and (4.13) that the magnetoelastic contributions to the thermodynamic quantities are determined by the MVI constants γ and ε_{ik}. The solid curves in Figs. 6–10 show the temperature dependence of the shear moduli c_{44} and $(c_{11} - c_{12})/4$, the bulk moduli B_M and B_H, and the coefficients of thermal expansion calculated from (3.8) and (3.10) with the values of γ and ε_{ik} given above. It is evident from the figures that the calculations explain not only the orders of magnitude of these quantities, but also their temperature dependence.

Before continuing the analysis, we discuss the details of the calculation. The temperature dependence of the shear moduli was calculated using the following consequence of (3.8):

$$\frac{1}{2}(c_{11} - c_{12}) = \frac{1}{2}(c_{11}^0 - c_{12}^0) + \frac{1}{2}(\varepsilon_{11} - \varepsilon_{12})M^2,$$

$$c_{44} = c_{44}^0 + \varepsilon_{44}M^2$$

and the numerical values of ε_{11}, ε_{12}, and ε_{44} given above.

The coefficient of linear expansion α^L was calculated from the formula

$$\alpha_L = \alpha_\Phi^L - \frac{2}{3}\gamma M B_M^{-1}\left(\frac{\partial M}{\partial T}\right)_P.$$

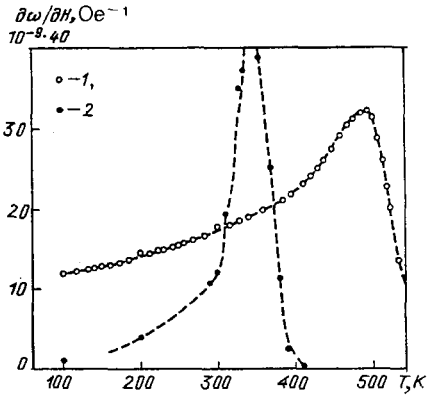

FIG. 4. Temperature dependence of the induced magnetostriction $\partial\omega/\partial H$ for disordered alloys: *1*) $Fe_{65}Ni_{35}$ (Ref. 18), *2*) $Fe_{72}Pt_{28}$ (Ref. 20).

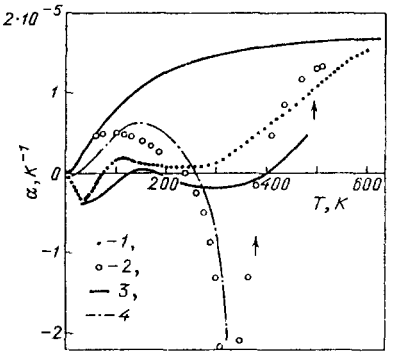

FIG. 6. Temperature dependence of the coefficient of linear expansion: *1*) experimental results of Ref. 18 for $Fe_{65}Ni_{35}$, *2*) experimental results of Ref. 20 for $Fe_{72}Pt_{28}$, *3*) α_{ph}^L (upper curve) and coefficient of linear expansion calculated from the formula given in the text for $Fe_{65}Ni_{35}$ (lower curve), *4*) calculated coefficient of linear expansion for $Fe_{72}Pt_{28}$.

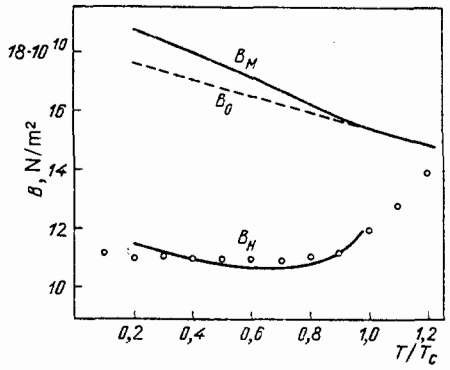

FIG. 7. Bulk modulus of $Fe_{65}Ni_{35}$ (Ref. 16).

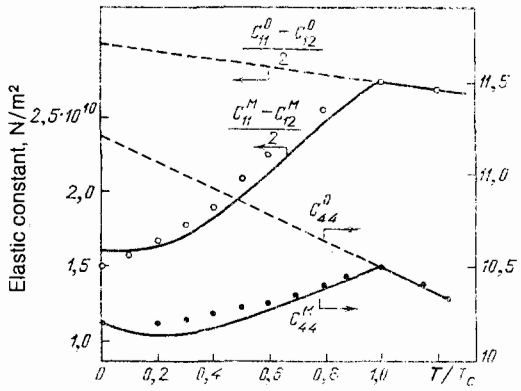

FIG. 9. Shear moduli of a $Fe_{65}Ni_{35}$ single crystal.[19]

We used $B_M \sim 1.8 \cdot 10^{12}$ erg/cm^3 (see Figs. 7 and 8) and the temperature dependence of the magnetization shown in Fig. 5. The value of the derivative $\partial M/\partial T$ was obtained by numerical differentiation of the graph $\sigma(T)$ in Fig. 5. The quantity α_{pl}^L shown by the upper solid curve in Fig. 6 is the phonon contribution to α^L in the Grüneisen approximation,[18] and is assumed to be the same for Fe–Ni and Fe–Pt Invars.

The bulk modulus was calculated from the equations

$$B_H = B_M - 4\gamma^2 M^2 \chi_V,$$

$$B_M = B_0 + \frac{1}{3}(c_{11} + 2c_{12})M^2.$$

If we compute χ_V from (3.10) using the experimental value of the high-field susceptibility (near saturation) for χ_P, the resulting value of $B_H - B_M$ is larger than the value measured experimentally by about a factor of two. We determined χ_V from the experimental data on $\partial\omega/\partial H$. Then (3.10) was used to compute χ_P. Finally χ_V was calculated from the relation $\chi_P^{-1} = \chi_V^{-1} - 4\gamma^2 M^2 B_M^{-1}$. The values of χ_V and χ_P calculated in this way are shown in Fig. 11. These values of χ_V were used to calculate B_H.

The close agreement between the calculated and experimental quantities shown in Figs. 6–10 cannot be accidental and demonstrates that the phenomenological theory of magnetovolume interactions can be used to explain Invar anomalies. Additional arguments in favor of the phenomenological theory are the above estimates of $\partial T_c/\partial P$, ΔB, and α above T_c, the explanation of the dispersion of the speed of sound, and the prediction of diffuse scattering by displacement fluctuations observed in Ref. 58. In our view, Masumoto in 1931 and Kornetskiĭ and Delinger in 1936 were the first to point out that the cause of the anomalies in Invar is the large positive spontaneous volume magnetostriction (for the history of the problem, see Ref. 1).

The longitudinal magnetic susceptibilities of Invar alloys are interesting. We see from Fig. 11 that when $T = (0\text{–}0.5)\,T_c$ the quantity χ_V in Fe–Ni Invar is approximately an order of magnitude larger than in Fe–Pt Invar. This is obviously a consequence of the magnetic inhomogeneities observed in Fe–Ni in Ref. 53 and studied in Refs. 54 and 60. Statistical fluctuations in composition lead to significant magnetic inhomogeneities in this alloy over a wide temperature range because of the strong dependence of the magnetization on composition.[61] This picture is consistent with the formula[62]

$$\chi_{\parallel} \sim \langle \delta M^2 \rangle \sim \left(\frac{\partial M}{\partial c}\right)^2 \langle \delta c^2 \rangle.$$

In the disordered alloy $Fe_{72}Pt_{28}$ the composition fluctuation $\langle \delta c^2 \rangle$ is approximately the same as in $Fe_{65}Ni_{35}$, but the dependence $M(c)$ is much weaker.[63] This is why $\chi_{\parallel}$ and the MVI effects are large only near T_c in this alloy, whereas in Fe–Ni they are also large for $T \approx (0.3\text{–}0.5)\,T_c$. The same conclusion can be drawn from the results of Ref. 64. The magnetic inhomogeneities in Fe-Ni Invar are the basic cause

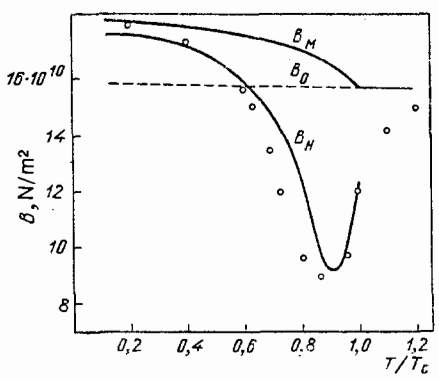

FIG. 8. Temperature dependence of the bulk modulus of $Fe_{72}Pt_{28}$ (Ref. 16).

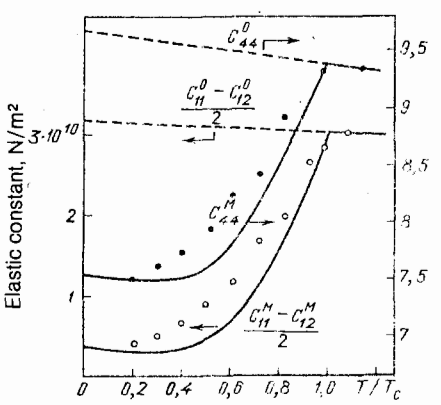

FIG. 10. Temperature dependence of the shear moduli of $Fe_{72}Pt_{28}$.

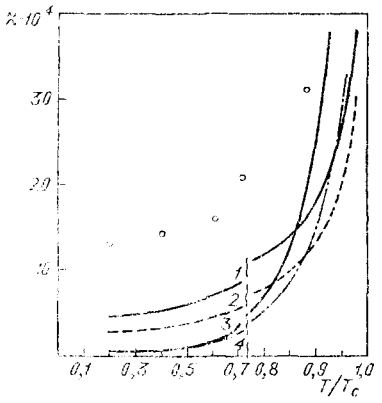

FIG. 11. Temperature dependence of the longitudinal susceptibility at constant volume χ_V (curves *2* and *4*) and at constant pressure χ_P (curves *1* and *3*) for $Fe_{65}Ni_{35}$ (curves *1* and *2*) and $Fe_{72}Pt_{28}$ (curves *3* and *4*). Circles: experimentally measured high-field susceptibility in $Fe_{65}Ni_{35}$ (Ref. 18).

of the different temperature dependence of the magnetization in $Fe_{65}Ni_{35}$ and $Fe_{72}Pt_{28}$ (Refs. 65 and 66).

In light of the above discussion, the role of magnetic inhomogeneities in the Invar problem is as follows. Large magnetovolume effects are observed in ferromagnets with $\gamma \sim 10^4$ erg/cm^{3}G^2, $M \sim 10^3$ G, and large longitudinal susceptibility $\chi_\parallel$. This follows from experiment and from the phenomenological theory of magnetovolume interactions. The equations given above show that magnetovolume effects also increase as the stiffness of the lattice decreases. In particular, the smaller is the value of the bulk modulus B_M, the larger is the value of $\omega \sim \gamma M^2 B_M^{-1}$.

In homogeneous Invars (ordered and disordered $Fe_{72}Pt_{28}$, Fe–Pd, and other alloys), the anomalies in α_H, B_H, and $\partial\omega/\partial H$ are observed near T_c because $\partial M/\partial T$ and χ_V are only large near T_c. In inhomogeneous alloys (such as $Fe_{65}Ni_{35}$; see Ref. 69), $\partial M/\partial T$ and χ_V are quite large far below T_c and hence α_H and B_H differ significantly from "normal" behavior at temperatures $\sim (0.3\text{–}0.5)\,T_c$.

Hence the magnetic inhomogeneities are not themselves the cause of the large magnetovolume effects, but they can strongly affect the temperature region in which anomalies in the thermodynamic quantities are observed. Therefore the effect of magnetic inhomogeneities is important in the practical application of Invars, when it is required to have some specified property of the thermal expansion or elastic constants in a certain temperature region.

The antiferromagnetism of γ-Fe observed in the literature[3] and its relation to Invars is connected with magnetic inhomogeneities. In Fe–Ni Invar, the centers of magnetic inhomogeneities (regions with a higher content of Fe atoms) transform into a state with short-range antiferromagnetic order (a spin glass state) when the temperature is lowered.[3,48] These centers play the role of defects in the magnetic structure and lead to low-temperature anomalies in the magnetic and other properties of $Fe_{65}Ni_{35}$. On the other hand, there are many alloys and compounds such as $Fe_{72}Pt_{28}$, MnAsSb (Ref. 67), YMn_2 (Ref. 68), and so on, in which inhomogeneities in the magnetic structure do not appear and there are no low-temperature anomalies. Nevertheless the magnetovolume effects are stronger in these compounds than in $Fe_{65}Ni_{35}$. Therefore one concludes that the antiferromagnetism of γ-Fe is not the only cause of the large magnetovolume effects. A final answer to the question of the relationship of antiferromagnetism in γ-Fe to the Invar problem must await further study. We only note that there are some compounds with large magnetovolume effects that do not contain iron atoms.[67]

ΔE effect of Invars and Elinvars

We consider the ΔE effect of Invar alloys. As before, we neglect the effect of the domain structure. The change in Young's modulus ΔE in passing into the ferromagnetic state is usually written in the form of a sum[70]

$$\Delta E = \Delta E_{\text{exch}} + \Delta E_\omega; \tag{7.1}$$

ΔE_ω is the change due to volume magnetostriction and was considered by Döring,[71] and ΔE_{exch} is the exchange contribution and is associated with the change in the interatomic forces in passing into the ferromagnetic state.

We discuss the limits of applicability of (7.1) and present explicit forms of the components of the sum. For polycrystalline samples the elastic constants can be expressed in terms of two independent variables: the bulk modulus B and the shear modulus G, where $B = (c_{11} + 2c_{12})/3$ and $G = (c_{11} - c_{12})/2 = c_{44}$. In exactly the same way, the second-order MVI constants are determined by the two independent quantities $(\varepsilon_{11} + 2\varepsilon_{12})/3 \equiv \varepsilon_B$ and $\varepsilon_{44} = (\varepsilon_{11} - \varepsilon_{12})/2 \equiv \varepsilon_G$.

The temperature dependence of the Young's modulus of polycrystalline Fe–Ni Invar can be obtained using the elastic constants of a single crystal, if one assumes that the bulk modulus of a single crystal is the same as that of a polycrystal and that the shear modulus of a polycrystal is given by the approximate expression

$$G = \frac{1}{2}\left[c_{44} + \frac{1}{2}(c_{11} - c_{12})\right]. \tag{7.2}$$

The calculated results of the Young's modulus

$$E = 9BG(3B + G)^{-1} \tag{7.3}$$

are shown in Fig. 12 by the solid curve. The fairly good agreement between the calculation and experiment suggests that (7.2) can be used for Fe–Ni Invar. The second-order MVI constants for polycrystals can be determined from the data on single crystals: $\varepsilon_B = (\varepsilon_{11} + 2\varepsilon_{12})/3$, $\varepsilon_G = [\varepsilon_{44} + (1/2)(\varepsilon_{11} - \varepsilon_{12})]/2$. We also note that the

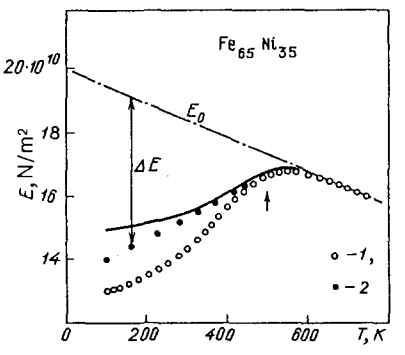

FIG. 12. Young's modulus of the disordered alloy $Fe_{65}Ni_{35}$ (Experimental results from Ref. 18): *1*) for $H = 0$, *2*) for $H = 500$ G.

magnetic contributions to the bulk modulus ΔB and the shear modulus ΔG of polycrystalline samples can be easily obtained from the expressions

$$\Delta B_H = \varepsilon_B M^2 - 4\gamma^2 M^2 \chi_V, \quad \Delta B_M = \varepsilon_B M^2,$$
$$\Delta G_H = \Delta G_M = \varepsilon_G M^2. \tag{7.4}$$

It follows from (7.3) that for the Young's modulus we have

$$\frac{\Delta E}{E} \approx \frac{1}{9}\frac{\Delta B}{B} + \frac{8}{9}\frac{\Delta G}{G}. \tag{7.5}$$

This last equation is obtained when $B = 8G/3$ (see Ref. 72) and is valid for $\Delta B/B \ll 1$, $\Delta G/G \ll 1$. The exact formula (7.3) should be used to calculate ΔE in the general case. We obtain from (7.4) and (7.5)

$$\Delta E_{exch} = \frac{E}{9}\left(\frac{\varepsilon_B}{B} + 8\frac{\varepsilon_G}{G}\right)M^2,$$

$$\Delta E_\omega = -\frac{4}{9}\gamma^2 M^2 \chi_V = -\frac{1}{9}B^2\left(\frac{\partial\omega}{\partial H}\right)^2 \chi_V^{-1}.$$

Once again we note that these equations are correct for the same conditions as (7.5).

The above discussion, in our opinion, applies directly to Elinvars as well. It was noted earlier that Elinvars are similar to Invar alloys in composition. For example, $Fe_{55}Ni_{45}$ is an Elinvar alloy. Analysis of the experimental data[1-4,40] shows that the MVI constants in Elinvars are several times smaller in absolute value than in Invars. Hence instead of a positive value of dE/dT for $T < T_c$, as in $Fe_{65}Ni_{35}$ Invar (see Fig. 12), the quantity dE/dT is nearly zero in a wide temperature region $T < T_c$ for $Fe_{55}Ni_{45}$ (Ref. 40). However, in order to determine the MVI constants in Elinvars more accurately and to compare their properties with the conclusions of the phenomenological theory, experimental information is necessary for polycrystalline and single-crystal Elinvars of the same composition, as was assumed in the case of $Fe_{65}Ni_{35}$ and $Fe_{72}Pt_{28}$. In addition, the numerical values of the second-order MVI constants in Elinvars are difficult to obtain reliably because the magnetic contribution to the elastic constants in Elinvars is smaller than in Invars.

This concludes our discussion of the phenomenological theory of magnetovolume interactions and its comparison with experiment. Although we have considered only the alloys $Fe_{65}Ni_{35}$ and $Fe_{72}Pt_{28}$ in our comparison with experiment, the dozens of ferromagnetic and antiferromagnetic compounds and alloys used as Invars and Elinvars have similar properties, i.e. their basic behavior can be explained using the phenomenological theory of magnetovolume interactions. The phenomenological theory described here can be used only for ferromagnetic Invars but it is not difficult to extend it to apply to antiferromagnetic compounds such as YMn_2 and also to antiferromagnetic alloys such as Fe–Mn–Ni, (Cr)FeMn, and so on.

Examples of unsolved problems are the problem of hidden magnetic excitations,[35] lattice dynamics for $K \neq 0$ (Ref. 43), the strong attenuation of spin waves,[48,73] and finally, the source of the strong magnetovolume interaction in Invars. The contribution of fluctuations to the thermodynamic quantities remains an unfinished problem. Apparently a more rigorous calculation of nonlinear effects is necessary.

Experimental confirmation would be desirable of the predictions of the phenomenological theory such as the effects of anharmonicity, parametric amplification of spin waves by sound, and diffraction effects.

8. CONCLUSION. ON THE MICROSCOPIC MECHANISM OF THE LARGE MAGNETOELASTIC INTERACTION IN INVARS

As a guide to a correct microscopic theory of magnetovolume interactions, we consider the formal analogy between the phenomenological theory considered above and the semi-phenomenological approach used to explain the properties of compounds with intermediate valency.[74] For example, the expressions for the spontaneous volume magnetostriction $\omega \sim \gamma M^2$ and the volume deformation in compounds with intermediate valency $\omega \sim n_f$ (n_f is the number of localized electrons) are the same if we put $n_f \sim \gamma M^2$. Since the physical properties of compounds with intermediate valency and Invars are similar (anomalies in the elastic constants, the coefficient of thermal expansion, and the dispersion of longitudinal sound), we assume that the charge density (valency) in Invars changes in the transition from the paramagnetic state to the ferromagnetic state. Many authors[7-9,75] have related the large magnetovolume effects in Invars to a change in the magnitude of the local magnetic moment. But in our opinion the large magnetovolume effect is caused not by a change in the local magnetic moment itself, but by the related change in the charge density, i.e. the quantity γM^2 may characterize the strong coupling between the spin and charge densities in Invars.

A similar idea on the change in the electron density of Invars has been mentioned by Zakharov.[2] The Weiss model[76] of a two-state Fe atom in Invar alloys is also consistent with this idea if it is assumed that the two states have different valencies. It is possible that Ref. 77 may be relevant to this question. There the longitudinal spin susceptibility of the electrons in a crystal was calculated and it was found that the spin and charge response functions are coupled.

Based on these ideas, we can obtain a qualitative picture of the change in the properties of Invar alloys when the temperature is lowered. Above the Curie point the local magnetic moment of Invar is somewhat smaller than in the magnetically ordered state. When we pass through the Curie point some of the collective electrons become localized on atoms, which increases the local magnetic moment and decreases the ionic charge. The change in the charge density accompanying the increase in the local magnetic moment and the magnetization leads to a change in the coupling forces between the atoms and therefore to a change in the volume and in the elastic properties.

Although the decrease in the local magnetic moment in Invars above T_c is a well established fact,[78,79] apparently the change in the charge density was studied only in Ref. 80. Therefore measurements of the charge density through T_c or T_N would be desirable in compounds such as $Fe_{72}Pt_{28}$ and YMn_2, where the charge density should vary in a narrow temperature region near $T_{c,N}$. A significant change in the electronic structure of Invars with temperature has been observed in photoelectron emission experiments.[81,82]

We also note that large magnetovolume effects should be expected near critical interatomic distances, i.e. distances separating the magnetically ordered and nonmagnetic states.[83] The same can be said for critical concentra-

tions.[66,84] These facts suggest that the coupling forces between atoms change significantly in the presence of local magnetic moments or magnetically ordered states.

An interesting property of magnetically ordered states in compounds with partial valency also suggests a dependence between the spin and charge density distributions. In helical magnetic structures observed in compounds such as $CeAl_2$, $CePb_3$, and CeSb the magnitude of the magnetic moment (not the direction, as in the usual case) varies sinusoidally.[85] Some of these questions were discussed in a recent international symposium.[86]

Therefore the nonrigidity of the magnetic moments, intermediate valency, and coupling between spin and charge fluctuations may be crucial for a microscopic theory of magnetoelastic interactions. The brief discussion given here shows that the Invar problem is related to the most fundamental questions of the theory of magnetism and the physics of the solid state.

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