Fluctuation-phonon approach to the theory of magnetism

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A new approach to the theory of the temperature dependence of the properties of magnetic materials with itinerant collectivized electrons is formulated. The effect which thermal phonon fluctuations exert on the magnetism via the magnetization dependence of the Debye temperature is taken into account. This magnetization dependence of the Debye temperature results from the particular form of the elastic modulus found from a common expression for the free energy at a constant magnetization density. New expressions are derived for the temperature dependence of the magnetization, the volume, and the thermal expansion coefficient of weak ferromagnets. A new interpretation is offered for the anomaly in the thermal expansion of an iron-nickel alloy of the Invar type. The baric derivatives and the isotopic effect are calculated. The phonon-induced temperature dependence of the magnetic susceptibility of paramagnets and ferromagnets is analyzed.

1. INTRODUCTION

The general expression for the free energy which we will be using below is

$$F_M(T,V,M)=F_0(V)+F_{eM}(T,V,M)+\Theta(V,M)f\left(\frac{T}{\Theta(V,M)}\right), \tag{1.1}$$

where $F_0(V)=F_M(0,V,0)$, F_{eM} is the magnetic component of the electron free energy, and $\Theta f(T/\Theta)$ is the lattice component of the free energy, which corresponds to the law of corresponding states.[1] An important point is that the Debye temperature Θ depends on not only the volume but also the magnetization density M. The reason for this M dependence can be seen from the dependence of the Debye temperature on the bulk modulus, which is known to depend on the magnetization density.[2] Here K_M, the bulk modulus at constant density, is given by the following expression:

$$K_M=V\left(\frac{\partial^2 F_M(0,V,M)}{\partial V^2}\right)_M=V\frac{d^2F_0}{\partial V^2}+V\left(\frac{\partial^2 F_{eM}(0,V,M)}{\partial V^2}\right)_M. \tag{1.2}$$

The temperature is assumed to be zero in this expression, which implies that we are ignoring the temperature dependence of quantities like $\Theta(V,M)$. The use of (1.1) and (1.2) along with an explicit expression found for F_{eM} in some way or other is the basic content of the self-consistent fluctuation-phonon approach to magnetism which we are presenting in this paper. We will restrict the discussion to weak ferromagnets with collectivized itinerant electrons, so that the consequences can be analyzed exhaustively.

We stress that an approach similar in its original form to our own was proposed by Kim *et al.*[3] However, they used a result of a dynamic theory for the bulk modulus, which differs with that found by the standard method, (1.2). It can be shown that the bulk modulus used in Ref. 3 corresponds to that which would be found in the standard thermodynamic approach, but at a constant magnetic field (more precisely, at a constant magnetic induction) B instead of at a constant magnetization density. Such a modulus K_B is known[4–6] to differ substantially from K_M, and for this reason the approach of Ref. 3 rules out the Stoner ground state of a weak ferromagnet with itinerant electrons. In contrast, the self-consistent fluctuation-phonon approach of the present paper retains the Stoner ground state of a ferromagnet at $T=0$, but it leads to a different temperature dependence for certain properties. To a significant extent, this temperature dependence is determined by thermal fluctuations of phonons, which are described by the function $\Theta f(T/\Theta)$ in the present paper.

2. MAGNETIC COMPONENT OF THE ELECTRON FREE ENERGY

To derive the electron magnetic component of the free energy of a ferromagnet we use Stoner's model (Refs. 7 and 8, for example), which is based on the two relations

$$M=\beta\int_0^\infty d\varepsilon\,\nu(\varepsilon)\left\{f_F\left(\varepsilon-\beta B+\frac{\psi}{\beta}M-\eta,T\right)-f_F\left(\varepsilon+\beta B-\frac{\psi}{\beta}M-\eta,T\right)\right\}, \tag{2.1}$$

$$\frac{N}{V}=\int_0^\infty d\varepsilon\,\nu(\varepsilon)\left\{f_F\left(\varepsilon-\beta B+\frac{\psi}{\beta}M-\eta,T\right)+f_F\left(\varepsilon+\beta B-\frac{\psi}{\beta}M-\eta,T\right)\right\}. \tag{2.2}$$

Here N is the total number of magnetic electrons, β is the magnetic moment of an electron, B is the magnetic induction, ψ is the exchange-interaction constant, $\nu(\varepsilon)$ is the density of electron energy states, and $f_F(\varepsilon,T)$ is the Fermi distribution function.

In the theory of weak ferromagnets with collectivized electrons, expansions in powers of B and M are carried out in (2.1) and (2.2). Determining the Fermi energy ε_F from

$$N/V=2\int_0^{\varepsilon_F} d\varepsilon\,\nu(\varepsilon), \tag{2.3}$$

finding the difference $\eta-\varepsilon_F$ from (2.2), and eliminating it from (2.1), we find

$$B=M\left\{\frac{1+2\psi\nu}{2\beta^2\nu}-\frac{(\pi\varkappa T)^2 o_1'}{12\beta^2\nu}\right\}+M^3\frac{\psi^3\nu^2 o_3'}{6\beta^4}. \tag{2.4}$$

Here $\nu=\nu(\varepsilon_F)$; the prime means differentiation with re-

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spect to the Fermi energy; $o_n = \nu'/\nu^n$, and $\varkappa$ is the Boltzmann constant.

Recalling the expression

$$B = \frac{1}{V}\left(\frac{\partial F_M}{\partial M}\right)_{T,V}, \tag{2.5}$$

we can write the following expression for the electron component of the magnetic part of the free energy:

$$F_{eM}(T, V, M) = VM^2\left\{\frac{1+2\psi\nu}{4\beta^2\nu} - \frac{(\pi\varkappa T)^2 o_1'}{24\beta^2\nu}\right\} + VM^4\frac{\psi^3\nu^2 o_3'}{24\beta^4}. \tag{2.6}$$

Finally, incorporating the free-energy component $-\frac{1}{2}\gamma(V)T^2$, where $\gamma(V)$ is the coefficient in the formula $C_e = \gamma(V)T$ for the magnetization-independent electron heat capacity, we find the following expression for the electron free energy of the metal:

$$F_{eM}(T, V, M) = F_{e0}(V) - \frac{1}{2}\gamma(V)T^2 + VM^2\left\{\frac{1+2\psi\nu}{4\beta^2\nu} - \frac{(\pi\varkappa T)^2 o_1'}{24\beta^2\nu}\right\} + VM^4\frac{\psi^3\nu^2 o_3'}{24\beta^4}. \tag{2.7}$$

We will use this expression below for both paramagnets and ferromagnets. If we use the inequality

$$|1+2\psi\nu| \ll 1, \tag{2.8}$$

which holds for weak ferromagnets and for strong paramagnets, we find that (2.7) takes the form (cf. Ref. 9)

$$F_{eM}(T, V, M) = F_{e0}(V) - \frac{1}{2}\gamma(V)T^2 + \frac{VM^2}{4\chi_0(V)}\left[1 - \frac{T^2}{T_0^2(V)} - \frac{M^2}{2M^2(0,0,V)}\right], \tag{2.9}$$

where we are using the standard notation

$$\chi_0(V) = \frac{\beta^2\nu}{1+2\psi\nu}, \quad T_0^2(V) = \frac{6(1+2\psi\nu)}{(\pi\varkappa)^2 o_1'},$$

$$M^2(0,0,V) = \frac{24\beta^2}{o_3'}(1+2\psi\nu). \tag{2.10}$$

In writing (2.6), (2.7), and (2.9), and in writing the term $\sim M^4$ we used the inequality $M \gg \beta^2\nu B$. The volume dependence of the coefficients in (2.10) results from the corresponding dependence of the exchange-interaction constant $\psi(V)$ and the energy-state density at the Fermi level, ν, and its derivatives. This dependence of ν on the volume arises (first) by virtue of condition (2.3) and (second) because of the volume dependence of the electron energy. Following Ref. 10, we assume

$$\varepsilon(\mathbf{p}, V) = W(V)E(\mathbf{p}), \tag{2.11}$$

where $W(V)$ is the volume-dependent width of the band. We then find

$$\nu = \frac{1}{W(V)}\mu\left(\frac{\varepsilon_F(V)}{W(V)}\right), \tag{2.12}$$

and Eq. (2.3) yields

$$N/2V = \int_0^{\varepsilon_F(V)/W(V)} dE\,\mu(E). \tag{2.13}$$

Finally, according to Ref. 11 we can assume $\ln W = r\ln V$, where we would have $r = -5/3$ in the case of a d band. By using Eq. (2.3) and relations (2.11)–(2.13) we are able to write the final results in a form which can be compared with model calculations.

3. THERMODYNAMIC RELATIONS

Shimizu[6] drew attention to the systematic use of thermodynamic relations in the microscopic theory. In particular, Shimizu contrasted and compared the quantities characterizing ferromagnets at a constant total magnetization of the ferromagnet and at a constant induction. In the construction of microscopic and semiphenomenological models in the theory of ferromagnetism, however, frequent use is made of such an order parameter as the magnetization density as a thermodynamic variable. This approach requires contrasting and comparing thermodynamic quantities at a constant magnetization density and at a constant induction. We make such a comparison in the present section of the paper.

Thinking of the magnetization density M as an order parameter in the theory of ferromagnetism, we find it convenient to use the free energy $F_M(T,V,M)$, a function of T, V, and M. Here

$$dF_M = -S\,dT - P_M\,dV + BV\,dM, \tag{3.1}$$

where $S = -(\partial F_M/\partial T)_{V,M}$ is the entropy, $B = V^{-1}\times(\partial F_M/\partial M)_{T,V}$ is the magnetic induction, and $P_M = -(\partial F_M/\partial V)_{T,M}$ is the pressure at a constant magnetization density. We can also write quantities which are determined by second derivatives of the free energy:

$$C_{V,M} = T\left(\frac{\partial S}{\partial T}\right)_{V,M} = -T\left(\frac{\partial^2 F_M}{\partial T^2}\right)_{V,M}, \tag{3.2}$$

the isochoric heat capacity at a constant magnetization density;

$$K_M = -V\left(\frac{\partial P_M}{\partial V}\right)_{T,M} = V\left(\frac{\partial^2 F_M}{\partial V^2}\right)_{T,M}, \tag{3.3}$$

the isothermal bulk modulus at a constant magnetization density; and

$$\chi_V = \left(\frac{\partial B}{\partial M}\right)^{-1}_{T,V} = \left[\frac{1}{V}\left(\frac{\partial^2 F_M}{\partial M^2}\right)_{T,V}\right]^{-1}, \tag{3.4}$$

the isothermal and isochoric magnetic susceptibility. The mixed second derivatives $(\partial^2 F_M/\partial T\partial M)_V$ and $(\partial^2 F_M/\partial V\partial M)_T$, also play a definite role in a description of experimentally observable results.

In experimental situations, the magnetization density is usually not constant. In contrast, conditions under which the magnetic induction B is constant are quite natural. In such a case it is convenient to use the free energy F_B,

$$F_B(T, V, B) = F_M(T, V, M) - BVM, \tag{3.5}$$

which is a function of the temperature, the volume, and the magnetic induction. The magnetization density M on the right side of (3.5) is also a function of T, V, and B, governed by Eq. (2.5). This approach naturally emphasizes the primacy of the free energy F_M. In accordance with (3.5) and (3.1) we have (cf. Ref. 6)

$$dF_B = -S\,dT - P\,dV - VM\,dB, \tag{3.6}$$

where $P = P_B = P_M + BM = -(\partial F_B/\partial V)_{T,B}$ is the pressure at constant induction. The following relations also arise

for the second derivatives of the free energy:

$$C_{V,B}=-T\left(\frac{\partial^2 F_B}{\partial T^2}\right)_{V,B}=C_{V,M}+\frac{TV}{\chi_V}\left(\frac{\partial M}{\partial T}\right)^2_{V,B}, \quad (3.7)$$

which is the isochoric heat capacity at a constant magnetic induction, and

$$K_B=-V\left(\frac{\partial P}{\partial V}\right)_{T,B}=V\left(\frac{\partial^2 F_B}{\partial V^2}\right)_{T,B}=K_M-\frac{V^2}{\chi_V}\left(\frac{\partial M}{\partial V}\right)^2_{T,B}, \quad (3.8)$$

which is the isothermal bulk modulus at a constant magnetic induction.

4. PHONON COMPONENT OF THE MAGNETIZATION-DEPENDENT PART OF THE FREE ENERGY

With Eq. (1.2) in mind, we write the bulk modulus at a constant magnetization density in the form

$$K_M=K_0+\Delta K_M, \quad (4.1)$$

where $K_0 = Vd^2F_0/dV^2$ corresponds to the value of K_M at $M=0$; using (2.7), we find the following expression for ΔK_M:

$$\Delta K_M=VM^2\frac{d^2}{dV^2}\left[\frac{V}{4\chi_0(V)}\right]\equiv\frac{\tau M^2}{4\beta^2\nu}, \quad (4.2)$$

where

$$\tau=\beta^2\nu V\frac{d^2}{dV^2}\left[\frac{V}{\chi_0(V)}\right] \quad (4.3)$$

is a dimensionless parameter. In particular, making use of the small value of the parameter (2.8), and applying (2.11)–(2.13) to the case of weak ferromagnets or strong paramagnets, we can write the following expression for τ:

$$\tau=-\frac{N^2o_3'}{4V^2}+\frac{No_2}{V}\frac{d\ln W}{d\ln V}-\frac{d^2\ln(\psi/W)}{d(\ln V)^2}-\frac{d\ln(\psi/W)}{d\ln V}\left[1+\frac{d\ln(\psi W)}{d\ln V}\right]. \quad (4.4)$$

We will use these expressions to determine the magnetization-density dependence of the Debye temperature $\Theta(V,M)$. We assume a constant derivative

$$d\ln\Theta/d\ln K=s; \quad (4.5)$$

this assumption corresponds, for example, to the case in which the longitudinal sound velocity is described by $u_l\sim K^{1/2}$, while the transverse sound velocity u_t does not depend on K. In this particular case we have

$$s=\{2[1+2(u_l/u_t)^3]\}^{-1}. \quad (4.6)$$

In a phenomenological treatment, τ and s can be regarded as parameters of the theory. For their product we use the notation $\bar\tau=\tau s$. It is not difficult to see that at small values of M^2 we have

$$\Theta(V,M)\approx\Theta(V)+\Theta'M^2=\Theta(1+\bar\tau M^2/4\beta^2\nu K_0). \quad (4.7)$$

This expression allows us to write the last term in (1.1) in the following approximate form:

$$\Theta(V,M)f\left(\frac{T}{\Theta(V,M)}\right)=\Theta(V)f\left(\frac{T}{\Theta(V)}\right)+\frac{\bar\tau M^2\Theta(V)}{4\beta^2\nu K_0}\varphi\left(\frac{T}{\Theta(V)}\right), \quad (4.8)$$

where

$$\varphi(x)=f(x)-xf'(x). \quad (4.9)$$

As a result, we can now write the following expression for the free energy of a weak ferromagnet found by expanding in powers of M^2:

$$F_M(T,V,M)=F_0(V)+\delta F(T,V,M)=F_0(V)-\frac{1}{2}\gamma(V)T^2+\Theta(V)f\left(\frac{T}{\Theta(V)}\right)+M^2\left\{\frac{V}{4\chi_0(V)}\left[1-\frac{T^2}{T_0^2(V)}\right]+\frac{\bar\tau\Theta(V)}{4\beta^2\nu K_0}\varphi\left(\frac{T}{\Theta(V)}\right)\right\}-\frac{VM^4}{8\chi_0(V)M^2(0,0,V)}. \quad (4.10)$$

We wish to stress that a temperature dependence arises in the magnetic part of the free energy not only because of the thermal spreading of the Fermi level ($\sim T^2$), as is usual in the Stoner approach, but also because of thermal phonon fluctuations [the appearance of the expression $\Theta\varphi(T/\Theta)$].

5. FERROMAGNETIC STATE; TEMPERATURE DEPENDENCE OF THE MAGNETIZATION

One of the most important consequences of expression (4.10) for the free energy is an equation which determines the dependence of the magnetization density M of the ferromagnet on the temperature T, the volume V, and the magnetic induction B. According to (2.5), we have the Belov-Arrott equation

$$\frac{2\chi_0 B}{M}+\frac{M^2}{M^2(0,0,V)}=1-\frac{T^2}{T_0^2}-\left(1-\frac{T_c^2}{T_0^2}\right)\frac{\varphi(T/\Theta)}{\varphi(T_c/\Theta)}. \quad (5.1)$$

In the case $B=0$, $T=0$, we evidently have $M=M(0,0,V)$. The Curie temperature T_c—the temperature at which the spontaneous magnetization vanishes in the absence of a magnetic induction ($B=0$)—in Eq. (5.1) is determined by the equation

$$\varphi\left(\frac{T_c}{\Theta}\right)=-\left(1-\frac{T_c^2}{T_0^2}\right)\frac{\beta^2\nu K_0 V}{\bar\tau\chi_0\Theta}. \quad (5.2)$$

The following asymptotic expressions will be useful below:

$$\Theta\varphi(T/\Theta)=C_{ph}T, \quad C_{ph}=\text{const} \quad \text{at} \quad T>\Theta, \quad (5.3)$$

$$\Theta\varphi(T/\Theta)=\tfrac{1}{4}C_{ph}(T)T, \quad C_{ph}(T)=C_0(T/\Theta)^3 \quad \text{at} \quad \Theta>T. \quad (5.4)$$

In general we would have $C_{ph}(T) = -(T/\Theta)f''(T/\Theta)$ here. From (5.2) and (5.3) we find the following expression for ferromagnets whose Curie temperature exceeds the Debye temperature ($T_c>\Theta$) and to which we apply the label "high-temperature," under the assumption $T_c \ll T_0$:

$$T_c=-\frac{\beta^2\nu K_0 V}{\bar\tau\chi_0 C_{ph}}=\frac{|1+2\psi\nu|K_0V}{\bar\tau C_{ph}}. \quad (5.5)$$

By way of comparison we recall that in the Stoner approach we have[7] $T_c\sim|1+2\psi\nu|^{1/2}$, while in the magnetic-fluctuation approach we have[12,13] $T_c\sim|1+2\psi\nu|^{3/4}$. A qualitatively different dependence arises for low-temperature ferromagnets, i.e., for ferromagnets with a Curie temperature lower than the Debye temperature ($T_c<\Theta$). In this case we find from (5.2) and (5.4)

$$T_c^4=-\frac{4\beta^2\nu K_0\Theta^3 V}{\bar\tau\chi_0 C_0}=\frac{4|1+2\psi\nu|K_0V\Theta^3}{\bar\tau C_0}, \quad (5.6)$$

where again we have assumed $T_c \ll T_0$.

It is obvious from (5.6) that there is an isotopic effect in

the dependence of the Curie temperature on m_i, the mass of the lattice atoms. According to (5.2) we have

$$\frac{d\ln T_c}{d\ln m_i}\approx -\frac{1}{2}\frac{d\ln T_c}{d\ln\Theta}=-\frac{1}{2}\left[1-\frac{\Theta\varphi(T_c/\Theta)}{T_c C_{ph}(T_c)}\right]. \quad (5.7)$$

The right side of (5.7) varies from 0 to $-3/8$. This result does not contradict the experimental results of Ref. 14.

At high temperatures $T>\Theta$, Eq. (5.1) takes the form

$$\frac{2\chi_0 B}{M}+\frac{M^2}{M^2(0,0,V)}=1-\frac{T}{T_c}, \quad T_c>\Theta. \quad (5.8)$$

A temperature dependence of this type is characteristic of (for example) the iron-nickel alloy[15] $Fe_{0.65}Ni_{0.35}$ of the Invar type over the wide temperature range $0.5\,T_c \lesssim T<T_c\approx 500$ K. The Debye temperature of this alloy is 350 K.

On the other hand, at temperatures below the Debye temperature, $T<\Theta$, Eq. (5.1) yields the following equation for a ferromagnet with a Curie temperature higher than its Debye temperature:

$$\frac{2\chi_0 B}{M}+\frac{M^2}{M^2(0,0,V)}=1-\frac{T^2}{T_0^2}-\frac{C_0 T^4}{4\Theta^3 C_{ph} T_c}. \quad (5.9)$$

Finally, we write Eq. (5.1) for the case in which the Curie temperature is lower than the Debye temperature:

$$\frac{2\chi_0 B}{M}+\frac{M^2}{M^2(0,0,V)}=1-\frac{T^2}{T_0^2}-\frac{T^4}{T_c^4}, \quad T_c<\Theta. \quad (5.10)$$

Equation (5.1) allows us to write the following expression for the magnetic susceptibility of a ferromagnet:

$$\chi_V=\left(\frac{\partial B}{\partial M}\right)^{-1}_{T,V}=-\frac{\chi_0 M^2(0,0,V)}{M^2(1+\xi)}, \quad (5.11)$$

where

$$\xi=-\frac{\chi_0 M^2(0,0,V)B}{M^3}. \quad (5.12)$$

In the limit $B=0$, in which Eq. (5.1) takes the form

$$\frac{M^2}{M^2(0,0,V)}=1-\frac{T^2}{T_0^2}-\frac{\varphi(T/\Theta)}{\varphi(T_c/\Theta)}, \quad T_c^2\ll T_0^2, \quad (5.13)$$

the magnetic susceptibility of a ferromagnet at constant volume has the temperature dependence

$$\chi_V=-\chi_0\left[1-\frac{T^2}{T_0^2}-\frac{\varphi(T/\Theta)}{\varphi(T_c/\Theta)}\right]^{-1}. \quad (5.14)$$

The limiting expressions for the temperature dependence of the combination in brackets here are the right sides of Eqs. (5.8), (5.9), and (5.10). The magnetic susceptibility χ_V is positive because of the inequality $\chi_0<0$, which holds for ferromagnets.

6. MAGNETOTHERMOELASTIC EFFECTS

To describe the change in the volume of a ferromagnet when the temperature and magnetic induction change, it is convenient to use the thermodynamic potential as a function of the pressure, the temperature, and the magnetic induction:

$$\Phi(P,\ T,\ B)=\Phi_0(P)+\delta F[T,\ V_0(P),\ M(T,\ B,\ V_0(P))], \quad (6.1)$$

where the small increment δF is given by (4.10), the volume $V_0(P)$ is given by the expression $V_0(P)=d\Phi_0(P)/dP$, and the magnetization density is given as a function of the temperature, the magnetic induction, and the volume by (5.1). Correspondingly, using (6.1), we find the following expression for the volume of a ferromagnet:

$$V=\left(\frac{\partial\Phi}{\partial P}\right)_{T,B}=V_0(P)+\frac{dV_0}{dP}\left[\left(\frac{\partial\delta F}{\partial V}\right)_{T,M}+\left(\frac{\partial\delta F}{\partial M}\right)_{T,V}\left(\frac{\partial M}{\partial V}\right)_{T,B}\right]_{V=V_0(P)} \quad (6.2)$$

Using the magnetization-independent bulk modulus $K_0=-(d\ln V_0/dP)^{-1}$ and the explicit expression for δF according to (4.10), we find from (6.2)

$$V=V_0(P)(1+\omega_T+\omega_M). \quad (6.3)$$

Here the relative volume change which is unrelated to the magnetism is given by (cf. Ref. 1)

$$\omega_T=\frac{1}{K_0}\left[\frac{1}{2}\frac{d\gamma}{dV_0}T^2-\frac{d\Theta(V_0)}{dV_0}\varphi\left(\frac{T}{\Theta}\right)\right], \quad (6.4)$$

and the magnetoelastic relative volume change ω_M due to the change in the magnetization is given by (cf. Ref. 6)

$$\omega_M\equiv\omega_M(T,\ B,\ P)=AM^2(T,\ B,\ V_0(P)), \quad (6.5)$$

where

$$A=-\frac{1}{4K_0}\frac{d}{dV_0}\left(\frac{V_0}{\chi_0(V_0)}\right). \quad (6.6)$$

For a weak ferromagnet we find the following approximate equation by virtue of the small value of (2.8), in accordance with (2.10):

$$-\frac{d\ln\chi_0(V)}{d\ln V}=\frac{d\ln M^2(0,0,V)}{d\ln V}. \quad (6.7)$$

We can thus write (6.6) as

$$A=-\frac{1}{2K_0\chi_0}\frac{d\ln M(0,0,V)}{d\ln V}=\frac{1}{2\chi_0}\frac{d\ln M(0,0,V_0(P))}{dP}. \quad (6.8)$$

Equation (6.7) becomes progressively more accurate as $d\ln M^2(0,0,V)/d\ln V$ increases. We might also note that the coefficient A is a directly measurable quantity. Also directly measurable are χ_0 and the baric derivative of the logarithm of the magnetization at $T=0$ and $B=0$.

The coefficient given by (6.8) also substantially determines the induced magnetostriction,

$$h=\frac{1}{V}\left(\frac{\partial V}{\partial B}\right)_{T,P}=-\frac{1}{V}\left(\frac{\partial MV}{\partial P}\right)_{T,B}\approx A\left(\frac{\partial M^2}{\partial B}\right)_{T,V_0(P)}=-\frac{2A\chi_0 M^2(0,0,V_0)}{M(1+\xi)}; \quad (6.9)$$

measurements of this quantity could also reveal the value of A.

Expression (6.5) has a temperature dependence unusual in comparison with that in the Stoner approach because of the unusual dependence of the magnetization, given by (5.1). The situation has been seen directly in an experiment[15] on the alloy $Fe_{0.65}Ni_{0.35}$, where the spontaneous magnetostriction ω_M was observed to have a linear temperature dependence in the region $0.5\,T_c<T<T_c$, in accordance with Eq. (5.8), which actually holds for $T>\Theta/4\approx 10^2$ K. Another manifestation of the new temperature dependence of the magnetization predicted by (5.1) arises in a consideration of the thermal expansion coefficient

$$\alpha_B = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_{B,P} = \alpha_e + \alpha_{ph}. \tag{6.10}$$

Here α_e corresponds to the temperature dependence which results from the thermal spreading of the electron Fermi level and is given by

$$\alpha_e = -T\left[\frac{1}{V_0}\frac{d\gamma}{dP} + \frac{2AM^2(0,0,V_0)}{T_0^2(1+\xi)}\right]. \tag{6.11}$$

This is the thermal expansion coefficient which arises in the Stoner theory. The second term in (6.10) corresponds to the phonon component and is given by

$$\alpha_{ph} = C_{ph}(T)\left[\frac{1}{V_0}\frac{d\ln\Theta}{dP} - \frac{AM^2(0,0,V_0)(1-T_c^2/T_0^2)}{\Theta\varphi(T_c/\Theta)(1+\xi)}\right]. \tag{6.12}$$

While the first term on the right side of (6.12) corresponds to the ordinary thermal expansion of a solid[1] due to the lattice, the second term, due to the magnetoelasticity, is a new effect—a manifestation of thermal phonon fluctuations in the magnetothermoelasticity of ferromagnets. To emphasize the importance of this effect, we consider the thermal expansion coefficient of the Invar alloy $Fe_{0.65}Ni_{0.35}$ at $T\sim T_c$. Since the thermal expansion is governed by phonons at these temperatures in the paramagnetic phase, we focus on expression (6.12). Using (5.3) and $B=0$, we can write that expression in the form

$$\alpha_{ph}(T) = \alpha_{ph}^{\text{II}}(T) + \Delta\alpha_{ph}^{M}(T), \tag{6.13}$$

where the first term in (6.13) is the same as the corresponding term in (6.12), and

$$\Delta\alpha_{ph}^{M}(T) = -C_{ph}(T)\frac{AM^2(0,0,V_0)}{T_cC_{ph}}\left(1-\frac{T_c^2}{T_0^2}\right). \tag{6.14}$$

The experimental data on this alloy[6,15,16] are $T_c = 495$ K and $AM^2(0,0,V_0) = 1.4$–1.9%. Accordingly, working from the experimental data we find $\Delta\alpha_{\text{ph}}^{M} = -(2.8$–$3.8)\ 10^{-5}$ K^{-1} for this alloy at the Curie temperature. Another possibility for determining $\Delta\alpha_{\text{ph}}^{M}$ arises if we estimate $AM^2(0,0,V_0)$ from the experimental value of the induced magnetostriction at $T=0$ which is given in the review in Ref. 6: $h = 5.5\cdot10^{-9}$ Oe^{-1} and $\chi_0 = -1.1\cdot10$ msu/g-mole, $M(0,0,V_0) = 9438$ msu/g-mole (Ref. 16). According to (6.9) we then have $AM^2(0,0,V_0) = -h[M(0,0,V_0)/2\chi_0] = 2.4\%$. This value gives us $\Delta\alpha_{\text{ph}}^{M}(T_c) = -4.8\cdot10^{-5}$ K^{-1}. On the other hand, the measured bulk thermal expansion coefficient in the paramagnetic phase for the alloy $Fe_{0.654}Ni_{0.346}$, of nearly the same composition, is $\alpha_{ph}^{p} \approx 3\cdot10^{-5}$ K^{-1} at $T=T_c$, $\alpha_{\text{ph}}^{p}\approx4.2\cdot10^{-5}$ K^{-1} at $T=600$ K, and $\alpha_{ph}^{p}\approx5.4\cdot10^{-5}$ K^{-1} at $T=700$ K, according to Ref. 17. For this alloy the two terms in (6.13) are evidently comparable. Furthermore, they cancel each other out to a large degree in the sum, and we believe that this effect corresponds to the "Invar anomaly" observed experimentally. It can be seen from these estimates that an accurate calculation of the degree of cancellation of the terms in (6.13) will require corresponding measurements from a single sample. We would like to stress that the two terms in (6.13)—the normal term and the thermomagnetoelastic term—depend on the temperature in the identical way, so that under conditions such that they cancel out one will observe the Invar anomaly over a broad temperature range.

In summary, the unusual aspect of the alloy $Fe_{1-x}Ni_x$ at $x\approx0.35$ which leads to the Invar property results from the following set of properties, according to the approach developed in this paper. First, the alloy has $T_c > \Theta$. Because of this relation, the thermal expansion is determined primarily by the phonon component, (6.13), at temperatures $T > \Theta/4\sim10^2$ K. Second, this alloy has a fairly large derivative[16] $d\ln M^2(0,0,V)/d\ln V \approx 10$ [by way of comparison, the values for pure Fe and Ni, for which the relation $T_c > \Theta$ also holds, are[16] $d\ln M^2(0,0,V)/d\ln V \approx 0.9$]. It is for this reason, as we showed above, that the components α_{ph}^{p} and $\Delta\alpha_{ph}^{M}$ are comparable in magnitude and cancel out in Invar. Third, the identical temperature dependence of α_{ph}^{p} and $\Delta\alpha_{ph}^{M}$ means that the two components will cancel out over a broad temperature range at $T<T_c$. At low temperatures, $T<\Theta/4\sim10^2$ K, where the phonon component ($\propto T^3$) is small, the electron component, (6.11), becomes important. This component could apparently lead to the observed[17] negative values of the thermal expansion coefficient of Invar at fairly low temperatures.

Finally, as can be seen from Sec. 3, the following quantities are important:

$$\left(\frac{\partial M}{\partial T}\right)_{B,V} = -\frac{M^2(0,0,V)}{M(1+\xi)}\left[\frac{T}{T_0^2} + \frac{C_{ph}(T)}{2\Theta\varphi(T_c/\Theta)}\left(1-\frac{T_c^2}{T_0^2}\right)\right], \tag{6.15}$$

$$\left(\frac{\partial^2 F_M}{\partial T\partial M}\right)_V = \left(-\frac{TV}{\chi_0 T_0^2} + \frac{\bar\tau C_{ph}(T)}{2\beta^2\nu K_0}\right)M, \tag{6.16}$$

$$\left(\frac{\partial^2 F_M}{\partial V\partial M}\right)_T = \frac{M}{\chi_0}\frac{d\ln M(0,0,V)}{d\ln V}, \tag{6.17}$$

$$\left(\frac{\partial M}{\partial V}\right)_{T,B} = \frac{M^2(0,0,V)}{VM(1+\xi)}\frac{d\ln M(0,0,V)}{d\ln V}. \tag{6.18}$$

The last two expressions, along with (3.8), give rise to the following relation between the bulk modulus at a constant magnetic induction and that at a constant magnetization density (cf. Refs. 18 and 19):

$$K_B - K_M = \frac{M^2(0,0,V)}{\chi_0(1+\xi)}\left(\frac{d\ln M(0,0,V)}{d\ln V}\right)^2. \tag{6.19}$$

The temperature dependence in the last equation arises exclusively from ξ. A comparison of this dependence[20] with experimental results[21] on the alloy $Fe_{0.65}Ni_{0.35}$ reveals that near the Curie temperature we should see, in addition to the effects which we have been discussing, some other effects, among which magnetic fluctuations should apparently play the leading role.[12,13]

We turn now to the baric dependence. We first note that the following relation obviously holds, according to (6.7):

$$-d\ln\chi_0(V_0)/dP = d\ln M(0,0,V_0)/dP. \tag{6.20}$$

Furthermore, the baric derivatives of the spontaneous magnetization at $T=0$ are frequently compared experimentally with the baric derivatives of the Curie temperature. In our analysis, a relation of this sort can be derived from (5.2) and (6.20). Specifically, when we make use of the small parameter in (2.8) we find

$$\frac{d\ln T_c}{dP} = \frac{2\Theta\varphi(T_c/\Theta)}{T_cC_{ph}(T_c)}\frac{d\ln M(0,0,V_0)}{dP}. \tag{6.21}$$

In this case the quantity

$$2\Theta\varphi(T_c/\Theta)/T_cC_{ph}(T_c) \tag{6.22}$$

varies between 2 at $T_c > \Theta$ and 0.5 at $T_c < \Theta$, according to (5.3) and (5.4). In particular, according to experimental data presented in Ref. 15 the value of the quantity in (6.22) for the alloy $Fe_{0.65}Ni_{0.35}$, with $T_c > \Theta$, is 1.7, while for the alloy $Zr(Fe_{0.3}Co_{0.7})_2$, with $T_c < \Theta$, the quantity in (6.22) is 0.44. Accordingly, these and similar experimental results may be connected to some extent with the fluctuation-phonon dependence of the quantity in (6.22).

To conclude this section of the paper we write an expression for the heat capacity at constant induction. According to (3.7), (6.15), and (6.16) we have

$$C_{V,B}=C_{V,M}-\frac{M^2(0,0,V)VT}{\chi_0(1+\xi)}\left[-\frac{T}{T_0^2}+\frac{\bar{\tau}\chi_0 C_{ph}(T)}{2\beta^2\nu K_0 V}\right]^2. \tag{6.23}$$

In particular, we find that in the limit $T > \Theta$ we have

$$C_{V,B}=C_{ph}-\frac{M^2(0,0,V)V}{4\chi_0(1+\xi)}\frac{T}{T_c^2}, \quad T_c^2 \ll T_0^2. \tag{6.24}$$

These expressions describe a discontinuity in the heat capacity at the Curie point at $B = 0$. According to (6.23), the magnitude of this discontinuity is

$$\Delta C=-\frac{M^2(0,0,V)VT_c}{\chi_0}\left[-\frac{T_c}{T_0^2}+\frac{\bar{\tau}C_{ph}(T_c)}{2(1+2\psi\nu)K_0V}\right]^2, \tag{6.25}$$

differing from the standard result[22] by the second (comparatively large) term in square brackets. It is interesting (cf. Ref. 23) to compare the discontinuity in the heat capacity with that in the thermal expansion coefficient. According to (6.25), (6.11), and (6.12) we have

$$\frac{\Delta\alpha}{\Delta C}=\frac{1}{V}\frac{d\ln M(0,0,V_0)}{dP}\left[\frac{T_c^2}{T_0^2}-\frac{\bar{\tau}\chi_0 C_{ph}(T_c)T_c}{2\beta^2\nu K_0 V}\right]^{-1}. \tag{6.26}$$

Assuming the condition $T_c^2 \ll T_0^2$, and incorporating the relation between baric derivatives given by (6.21), we find

$$\frac{\Delta\alpha}{\Delta C}=\frac{1}{V}\frac{2\Theta\varphi(T_c/\Theta)}{T_c C_{ph}(T_c)}\frac{d\ln M(0,0,V_0)}{dP}=\frac{1}{V}\frac{d\ln T_c}{dP}. \tag{6.27}$$

The right side of (6.27) corresponds to Eq. (2) of Ref. 23.

7. MAGNETIC SUSCEPTIBILITY OF PARAMAGNETS AND FERROMAGNETS IN THE PARAMAGNETIC PHASE

In the case of normal metals, in contrast with ferromagnets, Eq. (5.2) does not determine a Curie temperature. However, Eq. (5.1) holds, although the term $M^2/M^2(0,0,V)$ in this equation is small. Accordingly, we can use Eq. (5.1) to determine $\chi = M/B$, which is the paramagnetic susceptibility of a metal. We find

$$\chi=2\chi_0\left[1-\frac{T^2}{T_0^2}-\left(1-\frac{T_c^2}{T_0^2}\right)\frac{\varphi(T/\Theta)}{\varphi(T_c/\Theta)}\right]^{-1}. \tag{7.1}$$

This expression holds for both paramagnets and ferromagnets in the paramagnetic phase; in addition—an important point—it holds for not only weak ferromagnets but also strong ones. We begin with the low-temperature case, in which the Curie temperature is lower than the Debye temperature. For a low-temperature ferromagnet ($T_c < \Theta$) we then find

$$\chi=2\chi_0\left[1-\frac{T^2}{T_0^2}-\left(1-\frac{T_c^2}{T_0^2}\right)\frac{T^4}{T_c^4}\right]^{-1}, \quad T_c<T<\Theta, \tag{7.2}$$

$$\chi=2\chi_0\left[1-\frac{T^2}{T_0^2}-\left(1-\frac{T_c^2}{T_0^2}\right)\frac{4C_{ph}T}{C_{ph}(T_c)T_c}\right]^{-1}, \quad T_c<\Theta<T. \tag{7.3}$$

In addition, in the case of a high-temperature ferromagnet ($T_c > \Theta$), we have

$$\chi=2\chi_0\left[1-\frac{T^2}{T_0^2}-\left(1-\frac{T_c^2}{T_0^2}\right)\frac{T}{T_c}\right]^{-1}, \quad \Theta<T_c<T. \tag{7.4}$$

If $(T/T_0)^2$ is sufficiently small, (7.3) and (7.4) correspond to the Curie-Weiss law

$$\chi=-2\chi_0(T/T_W-1)^{-1}. \tag{7.5}$$

However, the values of T_W in these two cases are different. For the low-temperature ferromagnet, T_W may, under otherwise equal conditions, turn out to be smaller than the corresponding value for the high-temperature ferromagnet.

Let us look at the corresponding equations for paramagnets, with $\chi_0 > 0$ (or, equivalently, with $1 + 2\psi\nu > 0$). According to (5.2) it is more convenient in this case to write (7.1) as

$$\chi=2\chi_0\left[1-\frac{T^2}{T_0^2}+\frac{\bar{\tau}\chi_0(V)\Theta}{\beta^2\nu K_0 V}\varphi\left(\frac{T}{\Theta}\right)\right]^{-1}. \tag{7.6}$$

This expression takes the following form at temperatures below the Debye temperature:

$$\chi=2\chi_0[1-T^2/T_0^2+T^4/T_1^4]^{-1}, \tag{7.7}$$

where

$$T_1^4=4\beta^2\nu K_0 V\Theta^3/\bar{\tau}\chi_0(V)C_0, \quad \bar{\tau}>0. \tag{7.8}$$

We assume $T_0^2 > 0$. Since the relation $\chi_0(V) > 0$ holds for paramagnets, the right side of (7.7) is positive under the condition $T_i^2 < 2T_0^2$. While T_0^2 is always positive in the theory of Stoner ferromagnets, in our analysis it may or may not be positive. The case $T_0^2 > 0$, however, is interesting because in this case the magnetic susceptibility goes through a maximum as a function of the temperature according to (7.7), in agreement with experimental results on palladium at comparatively low temperatures.[24] The temperature at which this maximum is reached is

$$T_{max}=\frac{T_1^2}{\sqrt{2}\,T_0}=\varkappa\pi\left[\frac{K_0 V o_1'}{3\bar{\tau}C_0}\Theta^3\right]^{1/2}. \tag{7.9}$$

Near T_{max} as given by (7.9), the electron component ($\propto T^2$) and the phonon component ($\propto T^4$) of magnetic susceptibility (7.7) become comparable in magnitude. On the other hand, in the heat capacity of a metal these components become comparable[1] at temperatures $\sim\Theta/4$. In the case of palladium, the maximum in the susceptibility is seen at a temperature[24] $(T_{max})_{Pd} \approx 80$ K, close to $\Theta_{Pd}/4 \approx 69$ K.

In the opposite situation, with $T_0^2 < 0$, i.e., in the case

$$6(1+2\psi\nu)/o_1'<0, \tag{7.10}$$

the magnetic susceptibility falls off monotonically with increasing temperature. At temperatures below the Debye temperature we have

$$\chi=2\chi_0[1+T^2/|T_0|^2+T^4/T_1^4]^{-1}, \tag{7.11}$$

and at $\Theta_{Pd}/4 \approx 69$ K expression (7.6) gives us

$$\chi=2\chi_0[1+T^2/|T_0|^2+T/T_2]^{-1}, \tag{7.12}$$

where

$$T_2=\beta^2\nu K_0 V/\bar{\tau}\chi_0 C_{ph}, \quad \bar{\tau}>0. \tag{7.13}$$

Expressions (7.11) and (7.12) describe a monotonic decrease in the paramagnetic susceptibility with increasing temperature, in agreement with observations for many metals (see, e.g., Refs. 6 and 24). On the other hand, there are many metals which exhibit an increase in the paramagnetic susceptibility with increasing temperature.[6,24] This possibility can be seen easily, in particular, in (7.6) for $T>\Theta$, where this expression can be written

$$\chi=2\chi_0[1+T^2/|T_0|^2-T/T_3]^{-1}, \tag{7.14}$$

where

$$T_3=-\beta^2\nu K_0 V/\bar{\tau}\chi_0 C_{ph}. \tag{7.15}$$

The last expression may be positive if $\bar{\tau}<0$. If expression (7.14) is to correspond to a paramagnet in this case, the denominator in (7.14) must not vanish. This condition is satisfied at all times if $2T_3>|T_0|$. In the latter case, according to (7.14), the magnetic susceptibility increases with increasing temperature and reaches a maximum at

$$T_{max}=|T_0|^2/2T_3=-3\bar{\tau}C_{ph}/(\pi\varkappa)^2\sigma_1' K_0 V. \tag{7.16}$$

The temperature given by this expression is significantly higher than that given by (7.9) and may be related (for example) to the value of the temperature at which the maximum is seen in the magnetic susceptibility of rhodium.[25] However, a detailed comparison will presumably require an accurate account of the role of thermal expansion.[26]

8. CONCLUSION

The approach formulated above (certain aspects of which were summarized in Ref. 27) to the theoretical description of the effect of thermal phonon fluctuations on the magnetic properties of metals with itinerant collectivized electrons differs from the approach of Refs. 3 in that it makes use of the change which is caused in the elastic properties of a metal by the magnetization and which arises in a self-consistent treatment of the problem. A change of this sort is described by a common expression for the free energy, treated as a function of the order parameters (the magnetization density). The behavior caused by thermal phonon fluctuations corresponds to several properties which have been exhibited experimentally by magnetic materials and which have been difficult to interpret theoretically. On the other hand, we must stress that we have dealt here with a very simple self-consistent model of the effect of thermal phonons on magnetism. Turning this model into one more appropriate for a description of specific magnetic materials will require further analysis.

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