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Electron-phonon interaction mechanism of magnetovolume and magnetoelasticity effects in itinerant electron ferromagnets

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While the volume and elastic constants of a system are determined from its free energy, we note that the free energy of a metal consists of the electron part and the thermal phonon part, and that the phonon part also depends on magnetization. Starting from such an observation, we study the role of electron-phonon interaction in the volume and elastic behaviors of a ferromagnetic metal in the same spirit as we recently studied the role of electron-phonon interaction in determining the magnetic properties [D. J. Kim, Phys. Rev. Lett. **47**, 1213 (1981); Phys. Rev. B **25**, 6919 (1982); J. Appl. Phys. **55**, 2347 (1984)]. First, for the magnetovolume effect we find that in the ferromagnetic state of metals the phonon Grüneisen constant behaves in quite diverse ways sensitively depending upon their electronic structure near the Fermi surface, and can become negative to cause zero or negative thermal expansion. We propose that such behavior of the Grüneisen constant can be an important mechanism in the anomalous volume behavior of ferromagnetic metals including the Invars. Next, as for the magnetoelastic effect, in the ferromagnetic state the role of thermal phonons is found to be of secondary importance compared with that of electrons; the dominant cause of the magnetization dependence of elastic constants comes from that of electron energy as we previously noted. In the paramagnetic state, however, the temperature dependence of the elastic constant is found to be determined principally by the effect of thermal phonons.

I. INTRODUCTION

In some metallic ferromagnetics, the temperature dependence of volume in the temperature region below the Curie point T_C is quite different from that of ordinary nonmagnetic metals.[1] As is well known,[2] in the case of some Fe-Ni alloys the temperature dependence of the volume markedly deviates from the linear extrapolation of the higher-temperature behavior; thermal volume expansion coefficient can be very small, or even negative. Not all ferromagnetic metals behave like the Fe-Ni alloy, however; an example is pure Ni metal.[2] These anomalies of volume behavior are called the magnetovolume effect, and a system with a very small or negative thermal expansion coefficient, as is the case in some Fe-Ni alloys, is called an Invar.

In metallic ferromagnets, elastic constants also often show anomalous temperature dependence, as is observed in Fe-Ni alloys[3] and Fe-Pt alloys,[4] for instance. Not all ferromagnetic metals are anomalous in their elastic properties, however. Again, in Ni the elastic constant shows quite normal temperature dependence;[5] the elastic constant monotonously increases with decreasing temperature.

The mechanism of the anomalous magnetovolume effect and magnetoelasticity is not clear yet.[1,6] Note that this problem is directly related to the very mechanism of itinerant electron magnetism itself. The volume and elastic constant of a system are determined from how the free energy F of the system depends upon the volume. The equilibrium volume V of a system is determined from the condition

$$\frac{dF(V,M)}{dV}=0\ , \tag{1.1}$$

and the bulk modulus B or the compressibility κ of the system is calculated as

$$B=\frac{1}{\kappa}=V\frac{d^2F(V,M)}{dV^2}\ , \tag{1.2}$$

where

$$M=\frac{n_+-n_-}{n_++n_-}=\frac{n_+-n_-}{n} \tag{1.3}$$

is the (relative) magnetization of the metallic system, $n_\pm$ being the number of ± spin electrons. We do not explicitly show the temperature T dependence in F; note that in an equilibrium state, M is determined as the function of T and V, $M=M(T,V)$, and that M in $F(V,M)$ of Eqs. (1.1) and (1.2) is to be understood as such an equilibrium magnetization [see Eq. (1.4) below].

On the other hand, the magnetic properties of the system are determined from the dependence of the same free energy on the magnetization. The spontaneous magnetization in the ferromagnetic state is determined from the condition

$$\frac{dF(V,M)}{dM}=0\ , \tag{1.4}$$

and the magnetic susceptibility χ of the system in the paramagnetic state is calculated as

$$\frac{1}{\chi}=\left.\frac{d^2F(V,M)}{dM^2}\right|_{M=0}\ . \tag{1.5}$$

Here in Eqs. (1.4) and (1.5) again, V in F is to be understood as the equilibrium volume determined as the function of M or T.

Let us emphasize again that all the free energies appearing in Eqs. (1.1), (1.2), (1.4), and (1.5) are the same ones. Different models and approximations culminate in different results for $F(V,M)$. Thus the elucidation of magnetovolume effect and magnetoelasticity has served as a crucial test of various models and theories of itinerant electron magnetism. The mechanism of anomalous magnetovolume effect has been particularly intensely discussed from such a point.[7] More recently, a very sensitive dependence on volume of magnetism is noted for transition metals.[8]

Recently we pointed out the importance of the role of phonons in itinerant electron magnetism.[9] We showed, for instance, how the phonon effect can make the paramagnetic spin susceptibility of a metal Curie-Weiss-like. The starting point of our such theory was to note the fact that in a metal the free energy consists of the electron part F_{el} and the phonon part F_{ph},

$$F(V,M)=F_{\mathrm{el}}(V,M)+F_{\mathrm{ph}}(V,M) \tag{1.6}$$

and the F_{ph} also depends on M as well as on V. The dependence on M and V of F_{ph} comes from that of the phonon frequency $\omega_{\mathbf{q}}=\omega_{\mathbf{q}}(V,M)$ in

$$F_{\mathrm{ph}}=\sum_{\mathbf{q}}\{\tfrac{1}{2}\hbar\omega_{\mathbf{q}}+k_B T\ln[1-\exp(-\hbar\omega_{\mathbf{q}}/k_B T)]\} \ . \tag{1.7}$$

The magnetization dependence of the phonon frequency originates from the fact that the screening constant, which screens the bare phonon frequency $\Omega_{\mathbf{q}}$ to $\omega_{\mathbf{q}}$, changes with the spin splitting of the energy bands of the screening electrons. Thus we obtain[9,10]

$$\begin{aligned}\omega_{\mathbf{q}}^2&=\Omega_{\mathbf{q}}^2-|g(\mathbf{q})|^2\frac{\tilde{F}_{+}(\mathbf{q})+\tilde{F}_{-}(\mathbf{q})}{1+v(\mathbf{q})[\tilde{F}_{+}(\mathbf{q})+\tilde{F}_{-}(\mathbf{q})]}\\&=\left[\Omega_{\mathbf{q}}^2-\frac{|g(\mathbf{q})|^2}{v(\mathbf{q})}\right]+\frac{|g(\mathbf{q})|^2/v(\mathbf{q})}{1+v(\mathbf{q})[\tilde{F}_{+}(\mathbf{q})+\tilde{F}_{-}(\mathbf{q})]}\ ,\end{aligned} \tag{1.8}$$

where $g(\mathbf{q})$ is the electron-phonon interaction constant which is related to the ionic plasma frequency Ω_{pl} and the Coulomb interaction $v(\mathbf{q})=4\pi e^2/Vq^2$ as

$$|g(\mathbf{q})|^2/v(\mathbf{q})=\Omega_{\mathrm{pl}}^2 \tag{1.9}$$

in the jellium model,[11] and we defined the exchange-enhanced Lindhard function of ± spin electrons as

$$\tilde{F}_{\pm}(\mathbf{q})=\frac{F_{\pm}(\mathbf{q})}{1-\tilde{V}(\mathbf{q})F_{\pm}(\mathbf{q})}\ , \tag{1.10}$$

where $\tilde{V}(q)$ is the exchange interaction between electrons, and $F_{\pm}(\mathbf{q})$ is the ordinary Lindhard function

$$F_{\pm}(\mathbf{q})=-\sum_{\mathbf{k}}\frac{f(\varepsilon_{\mathbf{k}\pm})-f(\varepsilon_{\mathbf{k+q},\pm})}{\varepsilon_{\mathbf{k}\pm}-\varepsilon_{\mathbf{k+q},\pm}} \tag{1.11}$$

with the property

$$\begin{aligned}\lim_{\mathbf{q}\to 0}F_{\pm}(\mathbf{q})&=F_{\pm}(\mathbf{0})\\&=\int N_{\pm}(\varepsilon)\left[-\frac{\partial f(\varepsilon)}{\partial\varepsilon}\right]d\varepsilon\simeq N_{\pm}(0)\ ,\end{aligned} \tag{1.12}$$

where $\varepsilon_{\mathbf{k}\pm}$, $f(\varepsilon)$, and $N_{\pm}(0)$ are, respectively, the one-particle energy of an electron with wave number $\mathbf{k}$ and spin ±, the Fermi distribution, and the density of states at the Fermi surface of ± spin electrons. The magnetization dependence of ω_q and, accordingly, F_{ph} comes from that of $F_{\pm}(q)$ or $N_{\pm}(\varepsilon)$. If we neglect the effect of the exchange interaction $[\tilde{V}(q)=0]$, and consider only the paramagnetic state, where

$$F_{+}(\mathbf{q})=F_{-}(\mathbf{q})=F(\mathbf{q})\ . \tag{1.13}$$

Equation (1.8) reduces to the well-known textbook result.[12]

An important point to note concerning our free energy of Eqs. (1.6)–(1.8) is that it was explicitly derived starting from the microscopic Hamiltonian of a metallic electron-phonon system.[13] Note also that the free energy should be, and actually was, obtained as the function of given (variational) magnetization as is required in the Landau procedure such as Eqs. (1.1), (1.2), (1.4), and (1.5). Thus, the magnetization involved in Eqs. (1.8), (1.10)–(1.12), and, accordingly, in F_{ph}, as well as in F_{el}, is not an equilibrium magnetization; the equilibrium magnetization is to be determined from Eq. (1.4) with such free energy.

Now, in understanding the importance of the role of phonons in magnetism of metals, the fundamental point to note is that[9] although

$$O(F_{\mathrm{ph}}/F_{\mathrm{el}})\simeq O(\hbar\omega_D/\varepsilon_F)\simeq 10^{-2}\ , \tag{1.14}$$

ω_D and ε_F being, respectively, the phonon Debye frequency and the electron Fermi energy, the sizes of the changes in F_{ph} and F_{el} due to magnetization can be of the same order of magnitude,

$$\begin{aligned}&O(|F_{\mathrm{ph}}(V,M)-F_{\mathrm{ph}}(V,0)|)\\&\qquad\cong O(|F_{\mathrm{el}}(V,M)-F_{\mathrm{el}}(V,0)|)\ .\end{aligned} \tag{1.15}$$

In qualitatively understanding Eq. (1.15), let us consider energies E_{el} and E_{ph} in place of the free energies. At $T=0$ the phonon energy is given by that of the zero-point oscillation,

$$E_{\mathrm{ph}}=\tfrac{1}{2}\sum_{\mathbf{q}}\hbar\omega_{\mathbf{q}}=O(Nk_B\Theta_D)\ ,$$

where Θ_D is the Debye temperature and N is the total number of atoms in the system [see Eqs. (1.7) and (2.17)]. In a metal the interaction between ions is screened by conduction electrons. While the screening constant is proportional to the electronic density of states at the Fermi surface, by the spin splitting of the electron bands the electronic density of states at the Fermi surface can change by one order of magnitude. This implies

$$|\Theta_D(M_0)-\Theta_D(0)|\simeq O[\Theta_D(0)]\ ,$$

or

$$|E_{\mathrm{ph}}(V,M_0)-E_{\mathrm{ph}}(V,0)|/N\simeq O(k_B\Theta_D)\ ,$$

where M_0 is the maximum possible magnetization [see Eq. (2.11)]. On the other hand, for a ferromagnet we anticipate

$$|E_{\mathrm{el}}(V,M_0)-E_{\mathrm{el}}(V,0)|/n \simeq O(k_B T_C) ,$$

n being the total number of electrons, as can be explicitly shown.[9] Then, since generally $O(n) \simeq O(N)$ and $O(T_C) \simeq O(\Theta_D)$ we arrive at the result of Eq. (1.15).

We now show how our such theory also leads to a new way of understanding the diversified volume and elastic behavior of ferromagnetic metals.[14] What is required is simply to carry out the procedure of Eqs. (1.1) and (1.2) with exactly the same F with such F_{ph} as we used in discussing magnetic properties.

First, as for the magnetovolume effect, we may summarize various volume behaviors of metals for $T < T_C$ as in Fig. 1. All the previous theories[1,7] are then unanimous in assuming that the lattice or phonon effect would always cause the "normal" volume behavior of the dashed line, independent of magnetism. Any deviations from such "normal" behavior are attributed entirely to electrons. By treating the phonon effect with our $F_{\mathrm{ph}}(V,M)$ described in the above, however, we find that in the ferromagnetic state of a metal the phonon Grüneisen constant γ_D can behave in quite diverse ways sensitively depending upon the electronic structure; γ_D can take even a negative value. With such behavior of the phonon Grüneisen constant it is no longer justified to assume the phonon effect on volume always as the broken line of Fig. 1. Instead, depending upon the sign and magnitude of γ_D, the phonon effect on volume ΔV_{ph} [see Eq. (2.7)] can be quite diverse as illustrated in Fig. 2. Note that such phonon effect has enough size to account for actual observations such as summarized in Fig. 1. While the size of the magnetovolume effect is generally of the order of $\sim 1\%$ as illustrated in Figs. 1, the size of the phonon effect on volume is also of the same order of $\sim 1\%$ as indicated by Eq. (1.14).

Next, as for the mechanism of the anomalous temperature dependence of elastic constant, particularly for the ferromagnetic state, we already presented an extensive discussion by exploring how the screening of phonon frequency depends on the spin splitting of the conduction electron bands[15] (see Sec. IV). More recently,[16] however, we realized that such a previous result can be rederived alternatively by carrying out the procedure of Eq. (1.2) without including F_{ph}. Then a question arises: What would be the effect of including F_{ph} in Eq. (1.2)? We answer to this question in this paper. For the ferromagnetic state of a metal, fortunately, the contribution of F_{ph} to the dependence on magnetization or temperature of elastic constant turns out to be much smaller than that of F_{el}; thus our earlier conclusion[15] remains essentially valid as it is. For the elastic constant in the paramagnetic state, however, we find the contribution of F_{ph} is very important; in this temperature region the temperature dependence of the elastic constant is determined principally by the effects of F_{ph}. This new finding resolves the difficulty with our previous result[15] in understanding the temperature dependence of elastic constant for $T > T_C$.

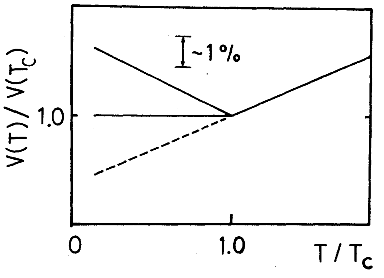

FIG. 1. Various characteristic volume behaviors of ferromagnetic metals below T_C.

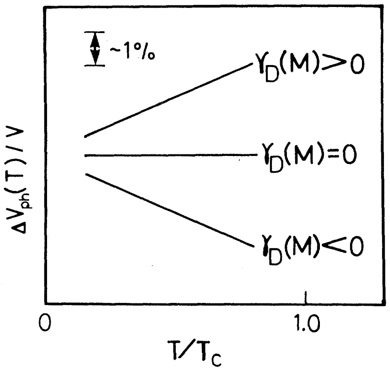

FIG. 2. The relation between phonon Grüneisen constant and the temperature dependence of the phonon effect on volume in the ferromagnetic state of a metal.

In concluding this Introduction, in response to the recent question raised by Zverev and Silin,[17] let us elaborate on the nature of our free energy, Eqs. (1.6)–(1.8), especially on that of F_{ph}. Although these authors fundamentally support our view on the importance of the role of phonons in magnetisms of metals, they claim our F_{ph} is calculated for a given magnetic induction but not for a given magnetization. In the following we show how their claim cannot be justified.

If we use the Debye approximation for the phonon frequency ω_{q}, the phonon free energy F_{ph} of Eq. (1.7) can be rewritten in terms of the bulk modulus or the Debye temperature [see Eqs. (2.16)–(2.20) below]. The magnetization dependence of F_{ph} then is dictated by that of the bulk modulus.

In their phenomenological phonon free energy Zverev and Silin use the bulk modulus as calculated by the procedure of Eq. (1.2) on the mean-field part of the electron energy. Let us call such a procedure of calculating elastic constants the total-energy approach. There is, however, an alternative method of calculating elastic constants. It is to obtain the sound velocity s from the dynamically derived phonon frequency ω_{q}, such as given in Eq. (1.8), as

$$\lim_{\mathrm{q}\to 0} \omega_{\mathrm{q}} = sq . \tag{1.16}$$

Then the bulk modulus is related to the sound velocity as

$$B = \frac{NM_i}{V} s^2 , \tag{1.17}$$

where M_i is the ionic mass. Let us call this method of calculating elastic constants the dynamical approach. If calculations are carried out exactly, we expect both approaches to give the same result. It is very well known, however, that if approximations are used, even if the nature of the approximations are similar, the results of the total-energy and the dynamical approaches can be quite different.[18] We have explicitly shown that it is only under some specific assumptions on the volume dependence of various physical quantities that the total-energy approach can reproduce the dynamical approach result of bulk modulus [see the discussion given below Eq. (2.13)].[16] Furthermore, it is not obvious at all which approach would give the better result on elastic constants.

Which bulk modulus, then, should we use for F_{ph} in the Debye approximation? If we start from the legitimately obtained result of Eqs. (1.6)–(1.8), we have no alternative but to use the dynamical one, as we have been doing. This is the main origin of the difference between our phonon free energy and that of Zverev and Silin.

Let us also reconfirm that our phonon free energy of Eqs. (1.7) and (1.8) is for a given magnetization as required in the Landau procedure such as Eqs. (1.1), (1.2), (1.4), and (1.5). The magnetization dependence of ω_{q} and, accordingly, F_{ph} is given solely through the magnetization dependence of $F_{\pm}(q)$ and $N_{\pm}(\varepsilon)$. Note that the magnetization dependence of F_{el} also is given entirely in terms of the same $F_{\pm}(q)$ and $N_{\pm}(\varepsilon)$. Thus, the magnetization dependence of F_{ph} can be treated exactly in the same way as in deriving the Stoner theory[19] from the magnetization dependence of F_{el}.

Also note that, unlike the case using phenomenological approach, with our result there can be no ambiguity concerning the contribution of the zero-point oscillation energy of phonons.

The organization of this paper is as follows. In Secs. II and III we discuss the contribution of the phonon effect to volume for the ferromagnetic and the paramagnetic states, respectively. The contribution of phonons to bulk modulus is discussed in Sec. IV and concluding remarks are given in Sec. V.

II. MAGNETOVOLUME EFFECT FOR $T < T_C$

In determining volume of an itinerant electron ferromagnet our whole task is to carry out the procedure of Eq. (1.1) with the free energy of Eq. (1.6). Note that F_{el}, or, more simply, the electron energy E_{el} is considered to consist of two terms, the one-particle energy of electrons E_0 and the exchange-correlation energy of electrons E_{ex}. For the uniform distribution of ionic and electronic charges (the jellium model) the three kinds of direct Coulomb interactions, among electrons, among ions, and between electrons and ions, cancel out. However, it is important to consider the energy E_ξ of the interaction between ions beyond that of the jellium point-charge ions. For convenience we include this E_ξ into F_{el} or E_{el}

$$F_{\text{el}}=F_0+F_{\text{ex}}+E_\xi \ . \tag{2.1}$$

It is well known that the role of attractive F_{ex} and that of repulsive F_0 are generally of equal importance in determining the volume.

For convenience, we rewrite Eq. (2.1) as

$$F_{\text{el}}(V,M)=F_{\text{el},m}(V,M)+\Delta F_{\text{el},c}(V,M) \ , \tag{2.2}$$

where $F_{\text{el},m}$ and $\Delta F_{\text{el},c}$ are, respectively, the mean-field and the higher-order correlation contributions to the electron free energy. The dominant contribution to $\Delta F_{\text{el},c}$ comes from F_{ex}. Then we define $V_0(M)$ from

$$\left.\frac{\partial F_{\text{el},m}(V,M)}{\partial V}\right|_{V=V_0(M)}=0 \ . \tag{2.3}$$

V_0 is the volume when there are neither $\Delta F_{\text{el},c}$ nor F_{ph} contributions. By the effect of $\Delta F_{\text{el},c}$ and F_{ph} the volume changes from V_0 to $V=V_0+\Delta V$ at each temperature or magnetization. $V_0(M)$ itself depends on magnetization and therefore, temperature. However, the dominant cause of the dependence on temperature or magnetization of volume is considered to come from F_{ph} and $\Delta F_{\text{el},c}$. Then since

$$|V(M_0)-V(0)|/V(0)\simeq|\Delta V(M_0)|/V(0)\simeq 10^{-2} \ , \tag{2.4}$$

as can be seen from Fig. 1, we may treat ΔV by perturbation theory. We know that the equilibrium magnetization also can be affected by the electron-phonon interaction,[9] as well as by electron correlation. In this paper, however, we neglect the effects of F_{ph} and $\Delta F_{\text{el},c}$ on magnetization. Then, by noting Eq. (2.3), we make the following expansion:

$$\begin{aligned}F_{\text{el},m}(V,M)=&F_{\text{el},m}[V_0(M),M]\\&+\frac{1}{2V_0(M)\kappa_{\text{el},m}(M)}\\&\times[V-V_0(M)]^2+\cdots\end{aligned} \tag{2.5}$$

where $\kappa_{\text{el},m}(M)$ is the mean-field approximation compressibility defined as

$$\begin{aligned}\frac{1}{\kappa_{\text{el},m}(M)}&=B_{\text{el},m}(M)\\&=V\left.\frac{d^2F_{\text{el},m}(V,M)}{dV^2}\right|_{V=V_0(M)} \ .\end{aligned} \tag{2.6}$$

The subscript el to κ and B refers to the fact that they are derived from F_{el} alone (see Sec. IV). Then by putting into Eq. (1.1) F_{ph} and F_{el} with this expanded $F_{\text{el},m}$, we obtain

$$\begin{aligned}\Delta V(M)/V_0(M)&=\kappa_{\text{el},m}(M)[P_{\text{ph}}(M)+P_{\text{el},c}(M)]\\&=[\Delta V_{\text{ph}}(M)+\Delta V_{\text{el},c}(M)]/V_0(M) \ ,\end{aligned} \tag{2.7}$$

with the pressures due to phonons and electron correlation, respectively,

$$P_{\rm ph}(M) = -\frac{d}{dV}F_{\rm ph}(V,M)\bigg|_{V=V_0(M)} ,$$
$$P_{{\rm el},c}(M) = -\frac{d}{dV}\Delta F_{{\rm el},c}(M)\bigg|_{V=V_0(M)} . \tag{2.8}$$

All the previous theories[1,7] on the magnetovolume effect unanimously assumed that in Eq. (2.7) the contribution of $\Delta V_{\rm ph}$ is always "normal" as in nonmagnetic metals. The origin of the anomalous volume behavior is entirely attributed to $\Delta V_{{\rm el},c}(M)$, although the details of electron correlation effects are different for different theories. In the following, by exploring the phonon effect on volume as described above, however, we find that the prevailing belief regarding the contribution of $\Delta V_{\rm ph}(M)$ to the volume behavior is not valid.

In pursuing $\Delta V_{\rm ph}(M)$ below, we discuss the bulk modulus $B_{{\rm el},m}(M)$ and the phonon pressure $P_{\rm ph}(M)$ separately in Secs. II A and II B and then in Sec. II C we present our phonon mechanism of magnetovolume effect for $T < T_C$.

A. Mean-field bulk modulus $B_{{\rm el},m}(M)$

We can obtain the bulk modulus by carrying out the procedure of Eq. (1.2) on the free energy of the form of Eq. (2.1). With the mean-field approximation for the electron energy as in Eq. (2.6), such a procedure was shown to lead to the result of familiar form[16] [see Eq. (1.17)],

$$B_{{\rm el},m}(M) = \frac{NM_i}{V}s(M)^2 , \tag{2.9}$$

where the magnetization dependence of $B_{{\rm el},m}$ comes from that of the sound velocity $s(M)$. If we normalize the sound velocity by the Bohm-Staver sound velocity of the jellium s_0, which is given as[11]

$$s_0^2 = V\Omega_{\rm pl}^2/8\pi e^2 N(0) , \tag{2.10}$$

where $N(0)$ is the electronic density of states per spin at the Fermi surface in the paramagnetic state, it is given as

$$\left[\frac{s(M)}{s_0}\right]^2 = \xi + \frac{2N(0)}{\dfrac{N_+(M)}{1-\tilde{V}N_+(M)} + \dfrac{N_-(M)}{1-\tilde{V}N_-(M)}} , \tag{2.11}$$

where $N_\pm(M)$ is the electronic density of states at the Fermi surface of ± spin electrons under magnetization M, and $\tilde{V} = \tilde{V}(\mathbf{q}=0)$ is the exchange interaction between electrons which appears in the Stoner spin susceptibility (with $\mu_B^2 = 1$) as

$$\chi_S = \frac{2N(0)}{1-\tilde{V}N(0)} . \tag{2.12}$$

Note that earlier we used $N_\pm(0)$ for $N_\pm(M)$ [see Eqs. (1.12)]. The parameter ξ is introduced to represent the effect of deviations from the jellium ions, which is contained in E_ξ of Eq. (2.1) in the following way:

$$\Omega_{\rm q}^2 - \Omega_{\rm pl}^2 = \xi s_0^2 q^2 . \tag{2.13}$$

In the pure jellium $\Omega_{\rm q} = \Omega_{\rm pl}$, and, therefore, $\xi = 0$. ξ is considered to be a constant of order unity.

Note the result of Eq. (2.11) was derived first with the dynamical approach by pursuing how the screening of the ion-ion interaction changes with magnetization,[15] namely, by the procedure of Eq. (1.16) for the phonon frequency of Eq. (1.8). Then, later[16] we found the same result can be obtained by the total-energy procedure of Eq. (2.6) if we assume the parabolic electron energy band and the volume dependence of the exchange interaction and the parameter ξ, respectively, as $\tilde{V} \propto 1/V$ and $(\xi s_0^2) \propto 1/V$. Here, however, we assume that if the procedure of Eq. (2.6) is more properly carried out it would reproduce the dynamical approach result of Eq. (2.9) and (2.11) beyond such limitations.

With Eq. (2.11), we rewrite Eq. (2.9) as

$$B_{{\rm el},m}(M) = \left[\frac{NM_i}{V}s_0^2\right]\left[\frac{s(M)}{s_0}\right]^2$$
$$\equiv B_0\left[\frac{s(M)}{s_0}\right]^2 . \tag{2.14}$$

Then, since $\Omega_{\rm pl}^2 = 4\pi e^2 NZ^2/VM_i$, with $NZ = n$, in Eq. (2.10), we have

$$B_0 = \frac{n^2}{2VN(0)} = \frac{2n\varepsilon_F}{3V} , \tag{2.15}$$

where the last expression is for the free-electron band where $N(0) = 3n/4\varepsilon_F$. Note that due to the result of Eq. (2.4) we may ignore the differences among $V(M)$, $V(0)$, $V_0(M)$, etc., and refer to them simply as V in an expression like Eq. (2.15).

$N_\pm(M)$ in Eq. (2.11) changes with the spin splitting of the electron bands. Since the size of the relative change of $N_\pm(M)$ can be generally of order unity, the change in sound velocity due to magnetization can also be of order unity unless $\xi \gg 1$. Such an observation led to the result of Eq. (1.15).

B. Phonon pressure $P_{\rm ph}(M)$ and Grüneisen constant $\gamma_D(M)$

The phonon free energy, which is required in calculating the phonon pressure from Eq. (2.8), is given in terms of the phonon frequency $\omega_{\rm q}(V,M)$ as in Eq. (1.7). Then, if we use the Debye approximation for the phonon frequency as

$$\omega_{\rm q}(V,M) = s(V,M)q , \tag{2.16}$$

this $s(V,M)$ is to be given by that of Eq. (2.11). Thus we obtain

$$F_{\rm ph}(V,M) = \tfrac{3}{8}N\hbar\omega_D(V,M) + Nk_BT\left\{\ln\left[1-\exp\left[-\frac{\Theta_D(V,M)}{T}\right]\right] - \frac{1}{3}D\left[\frac{\Theta_D(V,M)}{T}\right]\right\} , \tag{2.17}$$

where

$$D(x)=\frac{3}{x^3}\int_0^x dy\frac{y^3}{e^y-1} \tag{2.18}$$

is the Debye function and we set

$$\hbar s(V,M)q_D(V)=\hbar\omega_D(V,M)=k_B\Theta_D(V,M)\ , \tag{2.19}$$

q_D being the Debye wave number defined by

$$\frac{Vq_D^3}{6\pi^2}=N\ . \tag{2.20}$$

Note that since we are considering a jelliumlike model we have only longitudinal acoustic phonons.

By inserting Eq. (2.17) into Eq. (2.8), we obtain the pressure due to phonons as

$$P_{\text{ph}}(M)=\frac{Nk_B\Theta_D(M)}{V}\gamma_D(M)P\left[\frac{T}{\Theta_D(M)}\right]\ , \tag{2.21}$$

where we introduced the Grüneisen constant

$$\gamma_D(M)=-\frac{V}{\omega_D(M)}\frac{d\omega_D(V,M)}{dV}\bigg|_{V=V_0(M)} \tag{2.22}$$

and the function[9]

$$P\left[\frac{T}{\Theta_D}\right]=\frac{3}{8}+\frac{T}{\Theta_D}D\left[\frac{\Theta_D}{T}\right]$$

$$=\begin{cases}\dfrac{3}{8}+\dfrac{\pi^4}{5}\left[\dfrac{T}{\Theta_D}\right]^4 & \text{for } T\ll\Theta_D & (2.23)\\[2ex] \dfrac{T}{\Theta_D} & \text{for } T\gtrsim\Theta_D/3\ . & (2.24)\end{cases}$$

As for the Grüneisen constant of Eq. (2.22), in the ferromagnetic state it consists of two kinds of contributions

$$\gamma_D(M)=-\frac{V}{\omega_D(M)}\left[\frac{\partial\omega_D(V,M)}{\partial V}+\frac{\partial\omega_D(V,M)}{\partial M}\frac{dM}{dV}\right]$$

$$\equiv\gamma_D(M)_1+\gamma_D(M)_2\ . \tag{2.25}$$

Let us discuss $\gamma_D(M)_1$ and $\gamma_D(M)_2$ separately.

In calculating $\gamma_D(M)_1$ from Eq. (2.11), we are required to know how the various quantities appearing there would change with volume. Here we assume the following relations:

$$\frac{\partial}{\partial V}N_\sigma(M)=\frac{a}{V}N_\sigma(M)\ , \tag{2.26}$$

$$\frac{\partial}{\partial V}\tilde{V}=-\frac{b}{V}\tilde{V}\ , \tag{2.27}$$

$$\frac{\partial}{\partial V}(\xi s_0^2)=-\frac{c}{V}(\xi s_0^2) \tag{2.28}$$

with positive constants of order unity a, b, and c. Then from Eq. (2.11) we obtain

$$\gamma_D(M)_1=\frac{1}{3}+\frac{c}{2}+\left[\frac{s_0}{s(M)}\right]^2\left[(a-c)\frac{N(0)}{\tilde{N}_+(M)+\tilde{N}_-(M)}+(a-b)N(0)\tilde{V}\frac{\tilde{N}_+(M)^2+\tilde{N}_-(M)^2}{[\tilde{N}_+(M)+\tilde{N}_-(M)]^2}\right]\ , \tag{2.29}$$

where we put

$$\tilde{N}_\pm(M)=\frac{N_\pm(M)}{1-\tilde{V}N_\pm(M)}\ . \tag{2.30}$$

As for $\gamma_D(M)_2$, first we note,[16]

$$\frac{dM}{dV}=f\frac{M}{V}\tilde{V}\chi_{\text{HF}}(M)\ , \tag{2.31}$$

where

$$\chi_{\text{HF}}=4\left[\frac{1}{N_+(M)}+\frac{1}{N_-(M)}-2\tilde{V}\right]^{-1} \tag{2.32}$$

is the high field susceptibility (with $\mu_B^2=1$). Although the relation of Eq. (2.31) with $f=-\frac{1}{6}$ was derived for the parabolic electron energy dispersion, we assume it is valid beyond that limitation with a change in the numerical coefficient f. Since generally $f>0$ according to experiments,[19] in our later numerical calculation we assume the value of $f=\frac{1}{6}$.

Next, from Eqs. (2.16) and (2.11) we obtain

$$\frac{1}{\omega_D}\frac{\partial\omega_D}{\partial M}=\frac{1}{s(M)}\frac{\partial s(M)}{\partial M}$$

$$=\left[\frac{s_0}{s(M)}\right]^2 Y(M)\frac{n}{W} \tag{2.33}$$

with

$$Y(M)=-\tfrac{1}{2}N(0)W$$

$$\times\left[\frac{N'_+(M)/N_+(M)}{[1-\tilde{V}N_+(M)]^2}-\frac{N'_-(M)/N_-(M)}{[1-\tilde{V}N_-(M)]^2}\right]$$

$$\times[\tilde{N}_+(M)+\tilde{N}_-(M)]^{-2}\ , \tag{2.34}$$

where $N'_\pm(M)$ is the energy derivative of $N_\pm(M)$ and the electron band width W is introduced for convenience. Then from Eqs. (2.31) and (2.33) we have

$$\gamma_D(M)_2=-fn\tilde{V}MA/W\ , \tag{2.35}$$

with

$$A=\left[\frac{s_0}{s(M)}\right]^2 Y(M)\chi_{\mathrm{HF}}(M) \ . \tag{2.36}$$

Both $\gamma_D(M)_1$ and $\gamma_D(M)_2$, and, therefore, $\gamma_D(M)$ turn out to be quite complicated quantities. In Sec. II C we carry out some numerical calculations on these quantities. Before such numerical calculations, however, let us note that the quantity A of Eq. (2.36) is directly related to the external magnetic field dependence of sound velocity in the ferromagnetic state as,[9,20]

$$\frac{\Delta s(H)}{s}=A\frac{\mu_B H}{W} \ , \tag{2.37}$$

where $\Delta s(H)$ is the change in sound velocity due to a magnetic field H. We know that A can vary over quite a wide range. In Fe-Ni Invar, an external magnetic field of ~ 1 T, produces a change in the sound velocity of $\Delta s/s \simeq 1\%$.[3] This implies that in Fe-Ni $A/W \simeq 10^2$ eV^{-1}. On the other hand, in Ni under the same magnetic field of ~ 1 T, change in sound velocity was not observable,[5] implying there $|A/W| \ll 10^2$ eV^{-1}. If $f>0$ as experiments show, this situation causes to make $\gamma_D(M)$ of Fe-Ni much smaller than that of Ni. Note that such a difference in the behavior of the Grüneisen constant rightly coincides with the difference between the volume behaviors of Fe-Ni and Ni. Large A makes $\gamma_D(M)$ smaller or negative.

C. Magnetovolume effect through phonons for $T < T_C$: Negative phonon Grüneisen constant

From the results of Secs. II A and II B we have

$$\begin{aligned}\frac{\Delta V_{\mathrm{ph}}(M)}{V}&=\frac{1}{B_{\mathrm{el},m}(M)}P_{\mathrm{ph}}(M)\\&=\frac{Nk_B\Theta_D(M)}{V}\frac{1}{B_{\mathrm{el},m}(M)}\gamma_D(M)P\left[\frac{T}{\Theta_D(M)}\right] \ .\end{aligned} \tag{2.38}$$

Further from Eqs. (2.14), (2.15), (2.23), and (2.24) we rewrite Eq. (2.38) as

$$\frac{\Delta V_{\mathrm{ph}}(M)}{V}\cong\frac{3}{2}\left[\frac{N}{n}\right]\left[\frac{s_0}{s(M)}\right]^2\gamma_D(M)$$

$$\times\begin{cases}\dfrac{3}{8}\dfrac{k_B\Theta_D(M)}{\varepsilon_F} & \text{for } T\ll\Theta_D \quad (2.39)\\[2ex] \dfrac{k_BT}{\varepsilon_F} & \text{for } T\gtrsim\Theta_D/3 \ , \quad (2.40)\end{cases}$$

where we assumed the parabolic electron energy dispersion. First note that if $|\gamma_D|\simeq O(1)$ we have

$$|\Delta V_{\mathrm{ph}}/V|\simeq O(k_B\Theta_D/\varepsilon_F)\simeq 10^{-2} \ .$$

Thus, the effect of phonons is of enough size to account for the actually observed size of volume change in ferromagnetic metals.

How can it be possible, then, for $\Delta V_{\mathrm{ph}}(M)$ to become negative to cause negative thermal expansion? Since the bulk modulus should always be positive, it should be possible for $\gamma_D(M)$ to become negative. We show in the following, based on a numerical example, that actually is the case; it is possible to have all the cases of Fig. 2.

In numerically estimating the Grüneisen constant we are required to know the values of the parameters a, b, c, and f defined in Eqs. (2.26)–(2.28) and (2.31) besides the electronic density of states $N(\varepsilon)$ and the value of ξ. At present, however, we do not have any universally accepted values for those parameters a, b, c, and f. Remember that it is already a drastic simplification to assume the relations of Eqs. (2.26)–(2.28) to begin with.

In our numerical example, we assume $a=\frac{2}{3}$, $b=1$, and $c=1$ as in Ref. 16, $f=\frac{1}{6}$, and $\xi=2$. The value of $a=\frac{2}{3}$ corresponds to the free-electron-like energy dispersion. The value of $b=1$ comes from the assumption that $\tilde{V}(\mathbf{q})$ $[\tilde{V}=\tilde{V}(\mathbf{q}=\mathbf{0})]$ is the following form of the Fourier transform of the effective exchange potential between electrons:

$$\tilde{V}(\mathbf{q})=\frac{1}{V}\int \tilde{V}(\mathbf{r})e^{-i\mathbf{q}\cdot\mathbf{r}}d^3\mathbf{r} \ , \tag{2.41}$$

and that since $\tilde{V}(r)$ is of short-range the value of the integral would not be affected by a small change in the volume of the system; the value of $c=1$ also is similarly deduced. Note that there have been proposed a number of different values for the parameters a and b.[21,22] Heine,[21] for instance, proposed $a=\frac{5}{3}$ for $3d$ bands of transition metals.

As for the electronic density of states we use the following model:

$$N(\varepsilon)=\frac{6N}{W^3}\varepsilon(W-\varepsilon) \ , \tag{2.42}$$

which is illustrated in Fig. 3, where N is the number of atoms in the system and W is the bandwidth.

In calculating $\gamma_D(M)$, the equilibrium magnetization M is to be determined as the function of temperature for a given location of the Fermi energy ε_F in the band in the paramagnetic state, and for a given value of $\tilde{V}$ or $\bar{V}=\tilde{V}N(0)$. Here, however, for simplicity, we change M as the function of $\bar{V}$ for a given value of ε_F/W at $T=0$.

In Fig. 4 we present the result of our numerical calculation of the phonon Grüneisen constant for different locations of ε_F in the paramagnetic state, as the function of magnetization, M_0 being the maximum possible magnetizations for each case.

In Fig. 5 we show also how the role of $\gamma_D(M)$ dominates over that of bulk modulus $B_{\mathrm{el},m}(M)$ in determining the behavior of the phonon effect on the volume of a ferromagnetic metal. Note that, as we will see in Sec. IV, in the ferromagnetic state the observed bulk modulus is well represented by $B_{\mathrm{el},m}(M)$.

The result of Figs. 4 and 5 shows that the behavior of Grüneisen constant depends very sensitively on the electronic structure near the Fermi energy. When the Fermi energy in the paramagnetic state is located at the peak of the electronic density of states, with $\varepsilon_F/W=0.5$, $\gamma_D(M)$

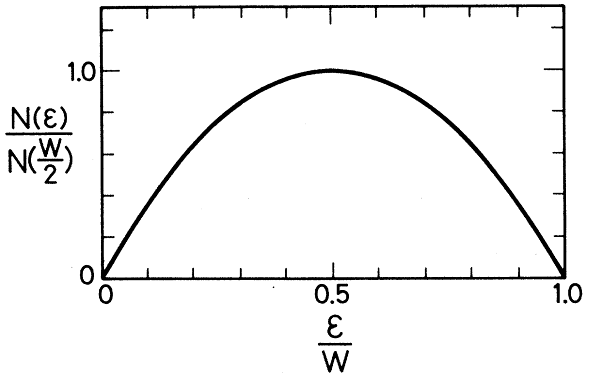

FIG. 3. The model electronic density of states of Eq. (2.42) to be used in the numerical calculation of Figs. 4, 5, and 6.

is positive and 0(1) except in the region $M/M_0 \simeq 1$ as can be seen from Fig. 4(a). With such $\gamma_D(M)$ we expect the phonon effect on volume to be normal. When the location of ε_F is away from the peak of the electronic density of states, $\gamma_D(M)$ strongly tends to be negative, as can be seen from Figs. 4(b)–4(d); in these cases the phonon contribution to thermal expansion coefficient becomes negative. The Invar behavior can be associated to the cases of Figs. 4(b)–4(d); the volume behavior of Ni corresponds to the case of Fig. 4(a). As will be summarized in Sec. IV, we previously[15] noted that the result of Eq. (2.11) can account for in the same way the difference between Fe-Ni and Ni in their characteristic magnetization dependence of sound velocity.

Concerning the results of Figs. 4 and 5 we should note that whereas $\gamma_D(M)$ crucially depends upon the parameters a, b, c, and f, we chose a particular set of values for them. Also, whereas $\gamma_D(M)$ and $[s(M)/s_0]^2$ depend very sensitively upon the electronic structure, we used the simplest possible model electronic density of states of Fig. 3. Thus, the result of Figs. 4 and 5 is of only qualitative nature. However, it seems to offer a sufficiently convincing evidence for the importance of considering the role of phonons in understanding the magnetovolume effect of itinerant electron ferromagnets.

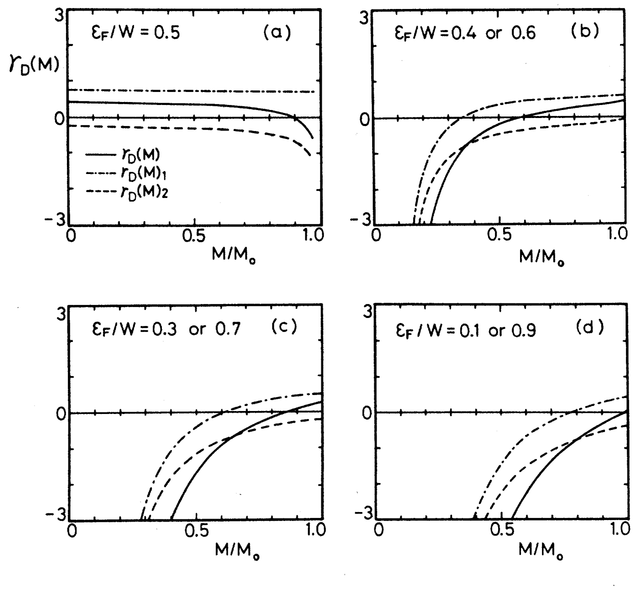

FIG. 4. The magnetization dependence of phonon Grüneisen constant calculated for various locations of the Fermi energy in the electronic density of states of Fig. 3 in the paramagnetic state.

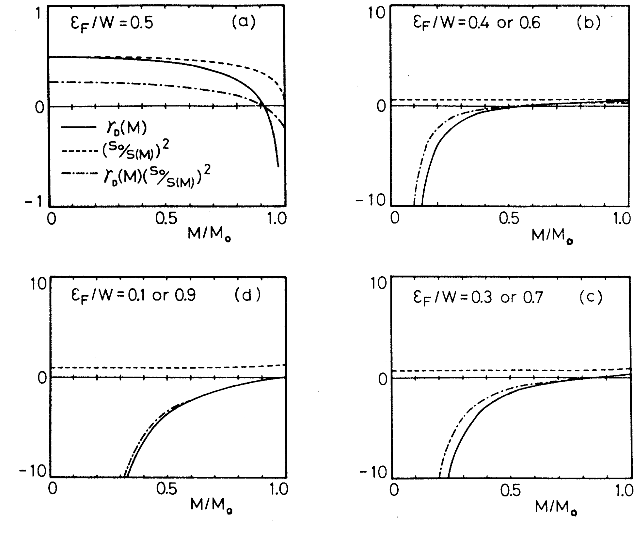

FIG. 5. The magnetization dependence of phonon Grüneisen constant, $[s_0/s(M)]^2$, to which compressibility is proportional, and their products calculated in the same way as in Fig. 4.

III. THERMAL EXPANSION IN THE PARAMAGNETIC STATE OF METALS

The formulation of the phonon effect on volume for $T > T_C$ is quite similar to that of the preceding section; we only have to replace M by T. Thus, corresponding to Eq. (2.7), for the phonon effect on volume we have

$$\frac{\Delta V_{\mathrm{ph}}(T)}{V} = \kappa_{\mathrm{el},m}(T) P_{\mathrm{ph}}(T) . \tag{3.1}$$

The meaning of notation is evident. The expressions for $\kappa_{\mathrm{el},m}(T)$ and $P_{\mathrm{ph}}(T)$ also are evident.

Here let us define the thermal volume expansion coefficient as

$$\beta = \frac{1}{V}\frac{dV(T)}{dT} = \beta_{\mathrm{el},m} + \beta_{\mathrm{ph}} + \beta_{\mathrm{el},c} . \tag{3.2}$$

The phonon contribution to thermal expansion coefficient corresponding to Eq. (3.1) is given as

$$\beta_{\mathrm{ph}} = \frac{1}{V}\frac{Nk_B}{B_{\mathrm{el},m}}\gamma_D , \tag{3.3}$$

where we assumed $T \gtrsim \Theta_D/3$ in Eq. (2.38) and neglected the temperature dependence in $B_{\mathrm{el},m}$ and γ_D. Note that in the paramagnetic state

$$B_{\mathrm{el},m} = \frac{n^2}{2VN(0)}[\xi + 1 - \tilde{V}N(0)] . \tag{3.4}$$

The mean-field electronic contribution to the thermal expansion $\beta_{\text{el},m}$, which represents the temperature dependence of $V_0(T)$, is smaller than β_{ph} by the factor of $k_B T/\varepsilon_F$ in the present temperature region (see Sec. IV). As for the contribution of electron correlation effect $\beta_{\text{el},c}$, we do not discuss it in this paper; we concentrate on β_{ph} as in the preceding section.

For $T > T_C$, the Grüneisen constant consists of only γ_{D1}. γ_{D2} vanishes for $M=0$. Thus, from Eq. (2.29) we have

$$\gamma_D = \tfrac{1}{3} + \tfrac{1}{2}c + \frac{1}{2}\left[\frac{s_0}{s}\right]^2 [(a-c) + \tilde{V}N(0)(c-b)] \ . \tag{3.5}$$

If we put $a = \frac{2}{3}$ and $b = c = 1$, as in Sec. II, Eq. (3.5) reduces to

$$\gamma_D = \frac{5}{6} - \frac{1}{6}\frac{1}{\xi + 1 - \overline{V}} \ . \tag{3.6}$$

Unless $\xi \ll 1$, we have $\gamma_D \simeq 1$, and the value of γ_D is not sensitive to the value of $\overline{V} = \tilde{V}N(0)$.

Thus, in the paramagnetic state, the dominant effect on β_{ph} of the exchange interaction between electrons is contained in the bulk modulus $B_{\text{el},m}$. If we assume thermal expansion is dominated by the phonon effect, the size of the exchange effect is estimated as

$$\begin{aligned} \frac{(\beta)_{\tilde{V}N(0)=1}}{(\beta)_{\tilde{V}N(0)=0}} &\cong \frac{(\beta_{\text{ph}})_{\tilde{V}N(0)=1}}{(\beta_{\text{ph}})_{\tilde{V}N(0)=0}} \\ &\simeq \frac{\xi+1}{\xi} \\ &= \begin{cases} 2 & \text{for } \xi = 1 \\ \frac{3}{2} & \text{for } \xi = 2 \ . \end{cases} \end{aligned} \tag{3.7}$$

In the paramagnetic state of a metal, while the thermal expansion coefficient is proportional to the electronic density of states at the Fermi surface through $B_{\text{el},m}$, the exchange effect can further enhance it by a factor of ~ 2. It seems that such conclusion is supported by the general trend of actual observations.[23]

IV. PHONON EFFECT ON MAGNETOELASTICITY

As already mentioned, earlier we derived the bulk modulus or the sound velocity of Eq. (2.11) for the ferromagnetic state of a metal from the result of Eq. (1.8) on the phonon frequency. According to this result, it is the magnetization dependence of the screening of the ion-ion interaction that is responsible for the magnetization dependence of bulk modulus or sound velocity.

Figure 6 is the result of numerical calculation on Eq. (2.11) carried out in the same way as for Figs. 4 and 5 with the same model electronic density of states of Fig. 3.[15] The result of Fig. 6 shows that the elastic behavior of a metal in the ferromagnetic state very sensitively reflects the electronic structure near the Fermi surface. Depending upon the location of the Fermi level within the band, the elastic constant can either increase or decrease with increasing magnetization. While the sound velocity of Eq. (2.11) consists of the contributions of ξ and the conduction electron terms, the latter can easily change by order unity. Note the important role of ξ; a large ξ ($\gg 1$) will mask the magnetization dependence in the electronic part. Although ξ also changes with temperature through thermal volume expansion, in the ferromagnetic state the size of such change in ξ is estimated to be much smaller than that of the electronic part; see Sec. IV A.

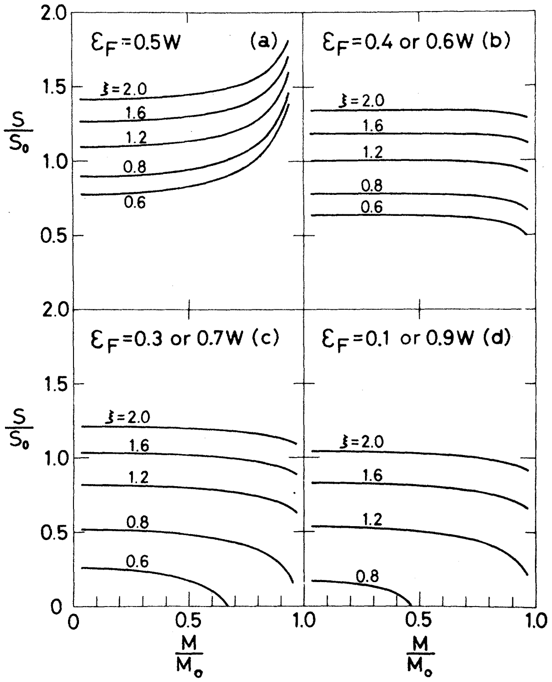

FIG. 6. The magnetization dependence of sound velocity calculated with Eq. (2.11) for the various locations of the Fermi energy in the electronic density of states of Fig. 3 in the paramagnetic state.

As we already noted, the elastic behavior below T_C of Fe-Ni alloys and pure Ni can be qualitatively understood, respectively, by Figs. 6(a), 6(c), and 6(d). How about the elastic behavior such as observed in Fe_3Pt[4]? For another model electronic density of states of Fig. 7, the result of Fig. 8 was obtained by the same procedure with Eq. (2.11).[24] Figure 8(d) seems to reproduce the characteristic behavior of Fe_3Pt qualitatively. Much better reproduction of the observation might be possible with more detailed consideration of the electronic structure and other factors. Thus, we may conclude that in principle, $B_{\text{el},m}(M)$, namely, the result of Eq. (1.8) or (2.11), can explain observed various characteristic elastic behavior in the ferromagnetic state of a metal.

How good is $B_{\text{el},m}$, then, in elucidating the elastic behavior of a metal in the paramagnetic state? Note that if we consider the temperature dependence in it, $B_{\text{el},m}$ of Eq. (3.4) for the paramagnetic state is rewritten as

$$\begin{aligned} B_{\text{el},m} &= B_0[\xi + 1 - \tilde{V}F(0)] \\ &= B_0(\xi + \chi_0/\chi_S) \ , \end{aligned} \tag{4.1}$$

where $\chi_0 = 2F(0) \simeq 2N(0)$ and χ_S are, respectively, the

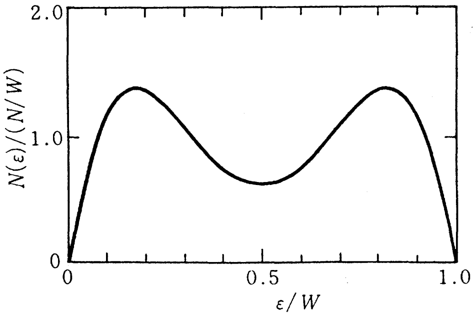

FIG. 7. The model electronic density of states to be used in the calculation of Fig. 8.

Pauli and the Stoner magnetic susceptibilities [see Eq. (2.12)], $F(0)$ being defined by Eqs. (1.12) and (1.13) and B_0 is given in Eq. (2.15). Unlike in the case of $T < T_C$, however, this result fails to reproduce the observed temperature dependence of the elastic constant for $T > T_C$ of ferromagnetic metals. In Ni the elastic constant decreases linearly with T for $T > T_C$.[5] In the Fe-Ni Invar, on the contrary, the elastic constant increases linearly with T over a fairly wide temperature region for $T > T_C$.[3] Such a linear temperature dependence cannot be derived from the temperature dependence of the Stoner susceptibility in Eq. (4.1).

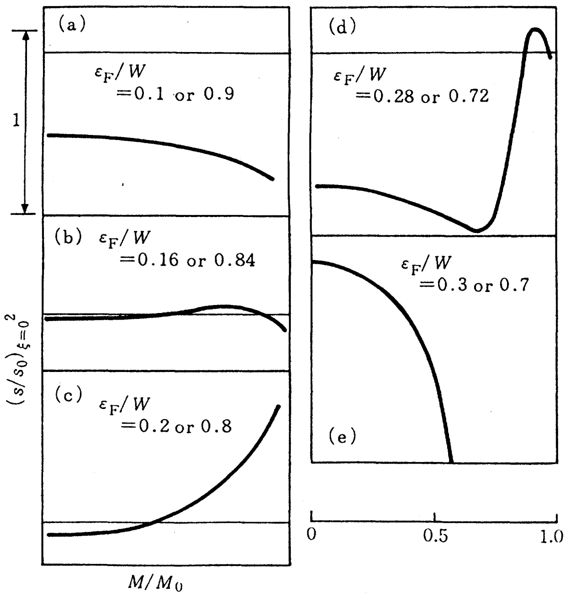

FIG. 8. The magnetization dependence of $[s(M)/s_0]^2$, to which the bulk modulus is proportional, calculated in the same way as in Fig. 6 for the model electronic density of states of Fig. 7. We put $\xi=0$ and the horizontal lines in each frame indicates the origin of the ordinate.

Also, the size of temperature dependence of $B_{\text{el},m}$ expected from the temperature dependence of $F(0)$ in the result of Eq. (4.1) is much too small compared to actual observations. If we note [see Eq. (1.12)]

$$F(0)=N(0)\left[1-\alpha\left[\frac{k_BT}{\varepsilon_F}\right]^2\right] \tag{4.2}$$

with $O(|\alpha|)=1$, we have

$$\frac{T}{B_{\text{el},m}}\left|\frac{dB_{\text{el},m}(T)}{dT}\right|=O\left[\frac{k_BT}{\varepsilon_F}\right]^2\simeq 10^{-8}T^2 , \tag{4.3}$$

where we assumed $\varepsilon_F \simeq 1$ eV. If we put $T\simeq T_C$ in Eq. (4.3), we have for $\text{Fe}_{68.5}\text{Ni}_{31.5}$ ($T_C\simeq 370$ K) and Ni ($T_C\simeq 630$ K), respectively, $\sim 2\times 10^{-3}$ and $\sim 4\times 10^{-3}$. The corresponding observed values for those systems are, respectively, ~ 0.4 (Ref. 3) and ~ 0.2 (Ref. 5). The discrepancy between the expectation from Eq. (4.2) and actual observation is a factor of $\sim 10^2$. Thus, as far as the temperature dependence in the paramagnetic state is concerned the result of Eq. (4.1) is quite insufficient; the situation is quite different from the case of the ferromagnetic state.

A possible way to remedy this difficulty might be to replace the Stoner susceptibility by a Curie-Weiss susceptibility in Eq. (4.1). However, not only is such a procedure not justifiable but also the sign of the observed linear T dependence is not always positive contrary to what is expected from such a replacement.

In summary, for $T < T_C$, $B_{\text{el},m}(M)$ can fairly well account for the observed various elastic behavior of itinerant electron ferromagnets. For $T > T_C$, however, $B_{\text{el},m}(T)$ completely fails to explain the observed various temperature dependence of the elastic constant.

Now, from our discussion in Secs. I, II, and III, we know that the bulk modulus is given as

$$\begin{aligned} B &= Vd^2(F_{\text{el},m}+\Delta F_{\text{el},c}+F_{\text{ph}})/dV^2 \\ &\equiv B_{\text{el},m}+B_{\text{el},c}+B_{\text{ph}} . \end{aligned} \tag{4.4}$$

Besides $B_{\text{el},m}$, we have to consider $B_{\text{el},c}$ and B_{ph}. As we have done for the magnetovolume effect in Secs. II and III, here we concentrate on the phonon effect on elastic constant, B_{ph}. Then we will find in Sec. IV B that for $T \gtrsim \Theta_D/3$, B_{ph} becomes proportional to T with either positive or negative sign, and with coefficient of enough size. There is, however, an additional source of linear T dependence in B of similar importance. It is the effect of the thermal volume expansion on $B_{\text{el},m}$. We first discuss this subject Sec. IV A. Finally in Sec. IV C we find that for the ferromagnetic state of a metal, the contribution of B_{ph} is much less important than that of $B_{\text{el},m}$. By supplementing $B_{\text{el},m}$ with such B_{ph} now we can account for the temperature dependence of bulk modulus of ferromagnetic metals both for $T < T_C$ and $T > T_C$.

A. The effect of thermal expansion on the bulk modulus in the paramagnetic state

The effect of thermal volume expansion ΔV on $B_{\text{el},m}$ of Eq. (4.1) may be written as

$$\Delta B_{\text{el},m}(T)/B_{\text{el},m}(T)=\delta\Delta V/V , \tag{4.5}$$

where for $T \gtrsim \Theta_D/3$ we have

$$\frac{\Delta V}{V}=\frac{\gamma_D N k_B}{V B_{\mathrm{el},m}}\Delta T \tag{4.6}$$

from Eq. (3.3), and

$$\delta = d\ln B_{\mathrm{el},m}/d\ln V$$
$$= -(a+1)-[(c-a)\xi+(a-b)\bar{V}]/(\xi+1-\bar{V}) , \tag{4.7}$$

the parameters a, b, and c being defined in Eqs. (2.26)–(2.28). By inserting Eq. (4.6) into Eq. (4.5) we obtain

$$dB_{\mathrm{el},m}(T)/dT=\delta\gamma_D N k_B/V \tag{4.8}$$

for the effect of thermal expansion on the temperature dependence of $B_{\mathrm{el},m}$.

As we have seen in Sec. III, γ_D is positive and $O(1)$ in the paramagnetic state of a metal. As for δ, from Eq. (4.7) it is likely to be negative with magnitude $\sim O(1)$. Thus Eq. (4.8) is estimated as

$$\left.\frac{T}{B_{\mathrm{el},m}(T)}\frac{dB_{\mathrm{el},m}(T)}{dT}\right|_{\text{therm. exp.}} \simeq -O\left(\frac{k_B T}{\varepsilon_F}\right) . \tag{4.8$'$}$$

Then, comparing to Eq. (4.3), we find that the effect of the thermal expansion on $B_{\mathrm{el},m}(T)$ is much larger than that of the thermal smearing of the Fermi distribution in $F(0)$ by the factor of $(\varepsilon_F/k_B T)$.

B. Phonon effect on bulk modulus in the paramagnetic state

If we note that in Eq. (4.4) F_{ph} of Eq. (2.17) depends on V only through the Debye frequency ω_D, the phonon contribution to bulk modulus is obtained as

$$\begin{aligned} B_{\mathrm{ph}} &= V\frac{d^2F_{\mathrm{ph}}}{dV^2} \\ &= V\frac{dF_{\mathrm{ph}}}{d\omega_D}\frac{d^2\omega_D}{dV^2}+V\frac{d^2F_{\mathrm{ph}}}{d\omega_D^2}\left[\frac{d\omega_D}{dV}\right]^2 \\ &= \frac{N\hbar\omega_D}{V}\left[\gamma_D' P(T/\Theta_D)-\gamma_D^2 Q\left[\frac{T}{\Theta_D}\right]\right] , \end{aligned} \tag{4.9}$$

where we put

$$\gamma_D'=\frac{V^2}{\omega_D}\frac{d^2\omega_D}{dV^2} \tag{4.10}$$

and

$$\begin{aligned} Q\left[\frac{T}{\Theta_D}\right] &\equiv -\frac{\omega_D}{N\hbar}\frac{d^2F_{\mathrm{ph}}}{d\omega_D^2} \\ &= 4\frac{T}{\Theta_D}D\left[\frac{\Theta_D}{T}\right]-\frac{3}{\exp(\Theta_D/T)-1} \\ &= \begin{cases} \dfrac{4\pi^4}{5}\left[\dfrac{T}{\Theta_D}\right]^4 & \text{for } T \ll \Theta_D \\ \dfrac{T}{\Theta_D} & \text{otherwise ,} \end{cases} \end{aligned} \tag{4.11}$$

where $D(x)$ is the Debye function of Eq. (2.18). γ_D is the Grüneisen constant in the paramagnetic state given by Eq. (3.6) and the function $P(x)$ is introduced in Eqs. (2.23) and (2.24).

As can be seen from Fig. 9 the function $Q(T/\Theta_D)$ defined in Eq. (4.11) behaves as T/Θ_D except at very low temperatures. As for γ_D', the second-order Grüneisen constant, we can derive an expression valid for $T<T_C$, as well as for $T>T_C$. Since the result is quite complicated, however, here we present only the result for $T>T_C$,

$$\begin{aligned} \gamma_D' &= 7\gamma_D/3-\gamma_D^2-\tfrac{2}{9}+c^2/2 \\ &\quad +\tfrac{1}{2}(s_0/s)^2[(a^2-c^2)+\bar{V}(c^2-b^2)] . \end{aligned} \tag{4.12}$$

As was with γ_D, it is difficult to estimate γ_D', but from Eq. (4.12) it appears that γ_D' can be either positive or negative with magnitude $O(1)$.

Thus, by going back to Eq. (4.9), for $T \gtrsim \Theta_D/3$ we find

$$B_{\mathrm{ph}}=Nk_B(\gamma_D'-\gamma_D^2)T/V . \tag{4.13}$$

If we compare this result with Eq. (4.8), we realize that the effect of the thermal expansion on $B_{\mathrm{el},m}$ is of the same size as that of B_{ph}. Summing $B_{\mathrm{el},m}$ and B_{ph}, for the bulk modulus in the paramagnetic state we have

$$\begin{aligned} B_{\mathrm{el},m}+B_{\mathrm{ph}} &= B_0(s/s_0)^2+dNk_B T/V \\ &= (2n\varepsilon_F/3V)[\xi+1-\tilde{V}F(0)] \\ &\quad +dNk_B T/V , \end{aligned} \tag{4.14}$$

with

$$d=\gamma_D\delta-\gamma_D^2+\gamma_D' . \tag{4.15}$$

In d of Eq. (4.15), as we already noted, δ is likely to be negative, while γ_D is likely to be positive; as for γ_D', it can be either positive or negative. Thus, if we note $O(|\gamma_D|)\simeq O(|\gamma_D'|)\simeq O(|\delta|)\simeq O(1)$, we find

$$d \simeq \pm O(1) . \tag{4.16}$$

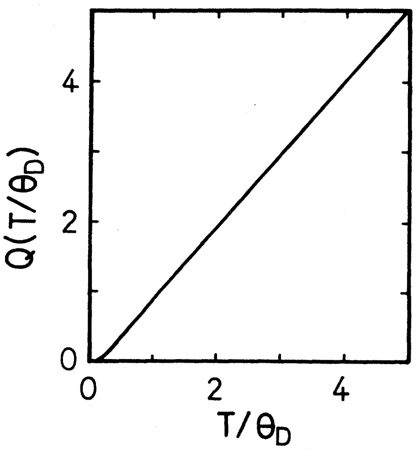

FIG. 9. The illustration of the function $Q(T/\Theta_D)$ defined in Eq. (4.17).

The linearly temperature-dependent contribution of Eq. (4.14) with d of Eq. (4.16) can now reproduce such observations as given in Refs. 3–5; $d \simeq O(1)$ for Fe-Ni Invar and $d \simeq -O(1)$ for Ni. In the case of Fe-Ni, at higher temperatures the temperature dependence of B begins to deviate from linear one and changes its sign. Such a behavior may be understood by considering the temperature dependence of B_{ph} more in detail by including that of $F(0)$, as we recently did in analyzing the temperature dependence of the magnetic susceptibility of $\mathrm{Y_2Ni_7}$.[25]

C. Phonon effect on the bulk modulus in the ferromagnetic state

At the beginning of this section we confirmed that in the ferromagnetic state of a metal the observed diversified temperature or magnetization dependence of an elastic constant can be satisfactorily accounted for by $B_{\mathrm{el},m}(M)$ or $[s(M)/s_0]^2$ of Eq. (2.11) alone. Such a situation suggests that in the ferromagnetic state the contribution of B_{ph} is much less important compared to that of $B_{\mathrm{el},m}$, quite contrary to the situation of the paramagnetic state. Let us show actually that is the case.

Note that Eq. (4.9) is valid also in the ferromagnetic state. Then we have

$$\begin{aligned} B_{\mathrm{el},m}+B_{\mathrm{ph}} &= B_0\left[\frac{s}{s_0}\right]^2 \\ &\quad + \frac{N\hbar\omega_D}{V}\left[\gamma_D' P\left[\frac{T}{\Theta_D}\right]-\gamma_D^2 Q\left[\frac{T}{\Theta_D}\right]\right] \\ &\equiv B_0\left[\frac{s}{s_0}\right]^2[1+R(T)] \end{aligned} \tag{4.17}$$

with

$$R=\frac{N\hbar\omega_D}{VB_0}\left[\frac{s_0}{s}\right]^2\left[\gamma_D' P\left[\frac{T}{\Theta_D}\right]-\gamma_D^2 Q\left[\frac{T}{\Theta_D}\right]\right], \tag{4.18}$$

where we did not include the effect of thermal expansion on $B_{\mathrm{el},m}$. If we note $P(T/\Theta_D) \cong Q(T/\Theta_D) \simeq O(1)$, and $(s/s_0)^2 \simeq O(1)$ we find

$$O(|R|)=O\left[\frac{N\hbar\omega_D}{VB_0}\right]\simeq O\left[\frac{\hbar\omega_D}{\varepsilon_F}\right]\simeq 10^{-2}\ . \tag{4.19}$$

Thus, in the ferromagnetic state of a metal, the temperature dependence of a bulk modulus is dominated by that of $B_{\mathrm{el},m}$ through $[s(M)/s_0]^2$; $[s(M)/s_0]^2$ can change by order unity in the ferromagnetic state. Consideration of the effect of thermal expansion, the size of its contribution being the same as that of R, does not change the above result.

Note that Eqs. (4.17)–(4.19) are valid in the paramagnetic state too; there, however, unlike in the ferromagnetic state, the temperature dependence of bulk modulus is dominated by that of B_{ph}; in the paramagnetic state, the temperature dependence of $B_{\mathrm{el},m}$ through $(s/s_0)^2$ is much smaller than that of B_{ph} as we saw in Sec. IV B

V. CONCLUDING REMARKS: ISOTOPE EFFECT ON $\Delta V_{\mathrm{ph}}(M)$

In this paper we have discussed on the role of phonons in the volume and elastic behaviors of ferromagnetic metals. We have shown the importance of treating phonons and electrons on the same footing in dealing with these subjects as was the case also in elucidating magnetic properties of metals.

All the previous theories[1,7] attributed the origin of anomalous volume behavior entirely to the effect of electron correlation; the phonon effect on volume ΔV_{ph} is assumed to always behave “normally” as in nonmagnetic metals. In this paper we have shown such prevailing premises are not justified. On the contrary, even with $\Delta V_{\mathrm{ph}}(M)$ alone, without considering the possible effect of electron correlation at all, we can understand the diverse characteristic volume behaviors of itinerant electron ferromagnets quite satisfactorily.

Our such finding in this paper seems to cast a rather grave question on the validity of the recent theories of itinerant electron ferromagnetism. All of those recent theories are based on the common ground of entirely neglecting the role of phonons such as we discussed in this paper. They attribute all the observed deviations from the mean-field approximation prediction entirely to the effect of electron correlation. If the phonon effect on magnetovolume, and magnetic properties in general, is as large as we have found, we have to fundamentally modify such understanding of itinerant electron magnetism.

Note that if the phonon effect is a dominant origin of the magnetovolume effect we may observe an isotope effect in the volume at low temperature of an itinerant electron ferromagnet. If we put the ionic mass and its isotopic difference, respectively, as M_i and δM_i, by assuming $\Theta_D \propto M_i^{-1/2}$ in Eq. (2.38), we have

$$\frac{\delta\Delta V_{\mathrm{ph}}(M_0)}{\Delta V_{\mathrm{ph}}(M_0)}=-\frac{1}{2}\frac{\delta M_i}{M_i} \tag{5.1}$$

for the change in the phonon effect on volume at $T \ll \Theta_D$. For an Invar system, since generally $|\Delta V_{\mathrm{ph}}(M_0)/V| \simeq 10^{-2}$, if $|\delta M_i/M_i| \simeq 10^{-2}$, we expect $|\delta\Delta V_{\mathrm{ph}}(M_0)/V| \simeq 10^{-4}$. An isotope effect of this magnitude on volume may be observable.

One feature of recent theories on magnetovolume effect, and itinerant electron ferromagnetism in general, is to require the presence of localized moments. We have shown, however, that if we consider the effect of the electron-phonon interaction, it is not necessary to have such localized moments. In this respect it would be very interesting if we can decide experimentally whether local moments are present or not in an itinerant electron ferromagnet. Such experiments are now beginning to be done.[26] The conclusion, however, appears not to be definitive yet.

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