Chapter 6
Magneto Volume Effect

6.1 Introduction

Magneto-volume effect is the phenomena resulting from the interplay between magnetism and volume change of crystals. For instance, the volume contraction by applying external pressure will change the magnitude of spontaneous moment as well as the critical temperature of magnetic transition. Conversely, the appearance of spontaneous magnetization also results in the volume expansion of crystals.

Volume change δV of crystals of magnetic origins is usually described by

$$\delta V = \kappa C_s M_0(T)^2 + \kappa C_h[M^2 - M_0^2(T)], \quad (6.1)$$

where $M_0(T)$ is the spontaneous magnetization. In this chapter, the compressibility of crystals is denoted by κ. The first term in (6.1) is called spontaneous magneto-striction. The second term, called forced magneto-striction, represents the volume change induced by applying external magnetic field. The ratio of the volume change δV to the volume V, i.e., $\omega \equiv \delta V/V$, is generally called volume-strain. In the theory of elasticity, the volume-strain ω is used rather than the volume change itself. Coefficients C_s and C_h in (6.1) are magneto-volume coupling constants (or magneto-elastic constant).

Among others, the invar alloys are known as an example in which the magneto-volume effect appears outstandingly. In these alloys, the thermal expansion arising from lattice vibrations is compensated by the volume contraction from this effect. As a consequence, they show almost no thermal expansion in some range of temperature. The property is utilized in various area of technological applications. Weak itinerant electron ferromagnets usually have large magneto-volume coupling constants, though their spontaneous magnetic moments are very small. For such reasons, a large number of pressure effect experiments had been made from the mid 1960s to 1980s.

The purpose of this chapter is to clarify the effects of spin fluctuations on the volume change of crystals based on the free energy in the preceding chapter.

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6.1.1 Thermal Expansion Due to Lattice Vibrations

Lattice vibrations is a typical example of boson excitations in crystals. It is known that the anharmonicity of lattice vibrations bring about the thermal expansion of crystals. Prior to our discussion on the magneto-volume effect and the involvement of spin fluctuations in this effect, it will be helpful for us to understand how the thermal expansion is derived from the lattice vibrations.

Thermodynamically, thermal expansion of crystals is derived from the volume derivative of the free energy. The free energy of the Debye model of the lattice vibrations is given by

$$\begin{aligned}\mathscr{F}(T,V) &= \frac{V}{2\kappa}\omega^2 + F_{\mathrm{lat}}(T,V),\\ F_{\mathrm{lat}}(T,V) &= \sum_{qs}\left[\frac{1}{2}\nu_{qs} + T\log(1-\mathrm{e}^{-\nu_{qs}/T})\right],\end{aligned} \tag{6.2}$$

as the sum of the elastic energy of the first term and the free energy $F_{\mathrm{lat}}(T,V)$ of the Debye mode. The anharmonicity is included as the volume dependence of the frequency ν_{qs} of phonons with wave vector q for component s. From the thermodynamic relation for the pressure p, the temperature dependence of the volume striction is given by

$$-p = \frac{\partial\mathscr{F}(T,V)}{\partial V} = \frac{1}{V}\frac{\partial\mathscr{F}(T,V)}{\partial\omega} = \frac{1}{\kappa}\omega + \frac{1}{V}\frac{\partial F_{\mathrm{lat}}(T,V)}{\partial\omega}, \tag{6.3}$$

$$\omega(T) = -\kappa p + \omega_{\mathrm{lat}}(T), \quad \omega_{\mathrm{lat}}(T) = -\frac{\kappa}{V}\frac{\partial F_{\mathrm{lat}}(T,V)}{\partial\omega}, \tag{6.4}$$

where the first term in (6.4) represents the volume contraction by pressure p. The second term of ω_{lat} is the thermal volume expansion originating from lattice vibrations. The volume dependence of phonon frequencies is usually defined by $\nu_{qs} \propto V^{-\gamma_{qs}}$. As the average of exponents γ_{qa}, the following Grüneisen parameter γ is defined by

$$\gamma = -\frac{\mathrm{d}\log\Theta_D}{\mathrm{d}\log V}, \tag{6.5}$$

where Θ_D is the Debye temperature.

According to the definition (6.3), the volume thermal expansion $\omega_{\mathrm{lat}}(T)$ is given by

$$\omega_{\mathrm{lat}}(T) = \kappa\sum_{qs}\frac{\partial\nu_{qs}}{\partial V}\left[\frac{1}{2}+n(\nu_{qs})\right] = \frac{\kappa\gamma}{V}\sum_{qs}\nu_{qs}\left[\frac{1}{2}+n(\nu_{qs})\right], \tag{6.6}$$

where $n(\nu_{qs}) = [\mathrm{e}^{\nu_{qs}/T}-1]^{-1}$. The volume thermal expansion coefficient is then evaluated by further differentiating (6.6) with respect to the temperature T:

$$
\begin{aligned}
\beta(T) &= \frac{\mathrm{d}\omega_{\mathrm{lat}}(T)}{\mathrm{d}T} = \frac{\kappa\gamma}{V}\sum_{qs} \nu_{qs}\frac{\partial}{\partial T}\left[\frac{1}{2} + n(\nu_{qs})\right] = \frac{\kappa\gamma}{V}\sum_{qs}\nu_{qs}\frac{\partial n(\nu_{qs})}{\partial T} \\
c_V(T) &= \frac{1}{V}\sum_{qs}\nu_{qs}\frac{\partial n(\nu_{qs})}{\partial T}
\end{aligned}
\tag{6.7}
$$

For isotropic crystals, the relation $\alpha(T) = \beta(T)/3$ is satisfied between the linear and volume thermal expansion coefficients, $\alpha(T)$ and $\beta(T)/3$. Thus the following Grüneisen relation is satisfied between the thermal expansion coefficient and the specific heat at constant volume:

$$
\alpha(T) = \frac{1}{3}\kappa\gamma c_V(T) \propto T^3 \quad \text{for } T/\Theta_D \ll 1 \tag{6.8}
$$

6.2 Stoner-Edwards-Wohlfarth Theory and its Correction

At the beginning, the magneto-volume effect is mainly understood by the Stoner-Edwards-Wohlfarth (SEW) theory. It is based on the Stoner-Wohlfarth (SW) free energy (1.53) in Chap. 1. Later in 1980, the theory was revised by Moriya and Usami [1] phenomenologically by including the contribution of spin fluctuations into the SEW free energy. We first show a brief outline of these theories.

6.2.1 SEW Theory of Magneto-Volume Effect

In the SEW theory, the following free energy is used for the derivation of the magneto-volume effect:

$$
\mathscr{F}(M,T,V) = \frac{V}{2\kappa}\omega^2 + F_0(T,V) + F_m(M,T,V), \tag{6.9}
$$

$$
F_m(M,T,V) = F_m(0,T,V) + \frac{1}{2}a(T,V)M^2 + \frac{1}{4}b(T,V)M^4 + \cdots. \tag{6.10}
$$

The second term $F_0(T,V)$ of (6.9) represents the contribution from the nonmagnetic degrees of freedom such as lattice vibrations. The third one $F_m(M,T,V)$ is the Stoner-Wohlfarth free energy (1.53), resulting from the band splitting of the conduction electron states. The SEW theory assumes that the coefficient of $a(T,V)$ in the SEW free energy (6.10) depends on the volume. The volume dependence of the higher coefficients, $b(T,V)$ for instance, are usually neglected. As is shown in (1.59), $a(T,V)$ in SW theory is given in terms of the single electron density of state $\rho(\varepsilon)$ at the Fermi energy and their energy derivatives, $\rho'(\varepsilon)$ and $\rho''(\varepsilon)$, as well as the intra-atomic electron-electron interaction I. The volume dependence of $a(T,V)$ is therefore determined by these quantities.

The volume strain is evaluated by the volume derivative of the free energy (6.9),

$$\begin{aligned}\omega(M,T) &= -\kappa p + \omega_0(T) + \omega_m(M,T),\\ \omega_0(T) &= -\frac{\kappa}{V}\frac{\partial F_0(T,V)}{\partial \omega},\\ \omega_m(M,T) &= -\frac{\kappa}{V}\frac{\partial F_m(T,V)}{\partial \omega} = -\frac{\kappa}{2V}\frac{\partial a(T,V)}{\partial \omega}M^2 + \cdots,\end{aligned} \tag{6.11}$$

where the terms $\omega_0(T)$ and $\omega_m(M,T)$ represent the nonmagnetic and magneto-volume contributions, respectively. The following consequences are derived from (6.11).

1. The spontaneous magneto-striction in the ordered phase
   In the absence of the external magnetic field, the magnetization M in (6.11) is replaced by the spontaneous moment $M_0(T)$. The first term of (6.1) is written by

$$\omega_m(T) = \frac{\kappa C}{V}M_0(T)^2, \quad C = -\frac{1}{2}\frac{\partial a(T,V)}{\partial \omega}. \tag{6.12}$$

   No spontaneous magneto-striction is present in the paramagnetic phase, because of the absence of the spontaneous magnetization $M_0(T)$. The magneto-volume coupling constant is given by the negative of the derivative of the coefficient $a(T,V)$ with respect to the strain ω.
2. The forced magneto-striction
   Increase of the magnetization induced by the external magnetic field also contributes to the volume expansion. An extra volume change from this effect in addition to (6.12) gives the second term of (6.1), i.e.,

$$\Delta\omega_m(M,T) = \frac{\kappa C}{V}[M^2 - M_0^2(T)]. \tag{6.13}$$

   Since the same coupling constant C appears, $C_s = C_h$ is satisfied. It can be applied in the paramagnetic phase, but with $M_0(T) = 0$.
3. Effects of volume change on the spontaneous magnetic moment and the critical temperature
   The conditions of (1.65) in Chap. 1 for the spontaneous magnetization in the ground state and its volume derivative give the following two relations:

$$\begin{aligned}&a(0,V) + b(0,V)M_0^2(0,V) = 0,\\ &\frac{\partial a(0,V)}{\partial \omega} + b(0,V)\frac{\partial M_0^2(0,V)}{\partial \omega} = 0\end{aligned} \tag{6.14}$$

   With the use of the definition of the coupling constant C in (6.12), the effect of the volume strain on the spontaneous magnetization is written in the form

$$\frac{\partial M_0^2(0, V)}{\partial \omega} = \frac{2C}{b(0, V)}. \quad (6.15)$$

We can also find the effect on the critical temperature T_c from the condition of $a(T_c, V) = 0$. The variation of this condition with respect to the change of volume strain $\delta\omega$ is given by

$$\left.\frac{\partial a(T, V)}{\partial T}\right|_{T=T_c} \delta T_c + \frac{\partial a(T, V)}{\partial \omega}\delta\omega = \frac{2a(0, V)}{T_c}\delta T_c - 2C\delta\omega = 0, \quad (6.16)$$

where we assume the volume dependence of $a(T, V) = a(0, V)[1 - T^2/T_c^2(V)]$. The temperature dependence of C is neglected. The ω derivative of $\log T_c$ is thus given by

$$\frac{1}{T_c}\frac{\partial T_c}{\partial \omega} = \frac{\partial \log T_c}{\partial \omega} = \frac{C}{a(0, V)} = \frac{C}{b(0, V)M_0^2(0, V)}. \quad (6.17)$$

From the comparison of (6.15) and (6.17), we are finally led to the following relation:

$$\frac{\partial \log M_0}{\partial \omega} = \frac{\partial \log T_c}{\partial \omega}. \quad (6.18)$$

4. Temperature dependence of the magneto-volume coupling constant
   In this theoretical framework, the value of C is expressed in the form

$$C = \frac{1}{4N\rho(\varepsilon_F)\mu_{\mathrm{B}}^2}\left[\frac{\partial\rho(\varepsilon_F)}{\partial\omega} + \bar{I}\frac{\partial I}{\partial\omega} + \frac{T^2}{T_F^2}\left(\frac{\partial\rho(\varepsilon_F)}{\partial\omega} + 2\frac{\partial T_F}{\partial\omega}\right)\right], \quad (6.19)$$

where $\bar{I} \equiv I\rho(\varepsilon_F)$. As shown in Chap. 1, $\rho(\varepsilon_F)$ and I represent the density of states at the Fermi energy and the repulsive Coulomb energy among conduction electrons. From the temperature dependence the Fermi distribution function, the above T^2-linear dependence is derived [2–4]. The volume dependence of the parameters $\rho(\varepsilon_F)$ and I are actually estimated numerically based on band structure calculations. In such studies, the $V^{-5/3}$ dependence of the d-electron band width by Heine [5] has been usually employed.

6.2.2 *Correction of the Free Energy of Spin Fluctuations*

Whereas the volume effect on the SW free energy is only taken in consideration in the SEW theory, Moriya and Usami [1] proposed its revision by including the contribution of spin fluctuations into their free energy. In place of the free energy $F_m(M, T, V)$ in (6.10), the following free energy is employed by them.

$$F_m(M,T,V) = \frac{1}{2}a(T,V)M^2 + \frac{1}{4}bM^4 + \frac{1}{2}\sum_{q\neq 0}\frac{1}{\chi(q)}\langle M_q \cdot M_{-q}\rangle + \cdots . \quad (6.20)$$

In addition to the coefficient $a(T,V)$ for the uniform ($q = 0$) component of the magnetization, they assumed the volume dependence of $\chi^{-1}(\mathbf{q})$ for the spatially modulated magnetization. Then the volume derivative of the free energy is given by

$$\begin{aligned}\frac{\partial F_m(M,T,V)}{\partial\omega} &\simeq -CM^2 + \frac{1}{2}\sum_{q\neq 0}\frac{\partial\chi^{-1}(q)}{\partial\omega}\langle M_q \cdot M_{-q}\rangle \\ &= -CM^2 - \sum_{q\neq 0} C_q \langle M_q \cdot M_{-q}\rangle . \end{aligned} \quad (6.21)$$

Only the thermal components of fluctuations are included as before. Then the wave-vector dependence of the coupling C_q is neglected, since thermal fluctuations around $q = 0$ are mainly excited usually. Thus the following result of the spontaneous volume striction is derived.

$$\omega_m(T) = \frac{\kappa C}{V}[M_0^2(T) + \xi^2(T)], \quad \xi^2(T) = \sum_q \langle \delta M_q \cdot \delta M_{-q}\rangle , \quad (6.22)$$

where $\xi^2(T)$ stands for the average of the thermal spin fluctuation amplitude squared.

According to Moriya and Usami, their theory of magneto-volume effect is different from the SEW theory in the following respects.

1. The presence of the spontaneous magneto-striction at the critical temperature. In the SEW theory, the spontaneous volume striction $\omega_m(0) = \kappa C M_0^2(0)/V$ below T_c disappears at $T = T_c$, i.e., $\omega_m(T_c) = 0$. Though both theories predict the same spontaneous volume striction $\omega_m(0)$ in the ground state, the volume striction in the MU theory remains finite, and its value is given by $\omega_m(T_c) = \kappa C\xi^2(T_c)/V$. If we notice the relation, $\xi^2(T_c) = 3M_0(0)^2/5$ satisfied between the thermal spin amplitude squared at $T = T_c$ and the spontaneous magnetization squared in the ground state, the volume contraction in the MU theory from the ground state to the critical point remains $2/5$ of the value in the SEW theory.
2. The presence of the magnetic thermal expansion in the paramagnetic phase. Although no thermal volume expansion of the magnetic origin is present in the SEW theory, the MU theory predicts the presence of the thermal volume expansion in the paramagnetic phase that results from the thermal spin fluctuation amplitude $\xi^2(T)$ in (6.22). It shows the T-linear increase with increasing temperature in the region where the Curie–Weiss law behavior of magnetic susceptibility is observed.

To exhibit a qualitative difference, the temperature dependence of thermal volume expansions predicted by these two theories is shown in Fig. 6.1. From the analysis of thermal expansion measurements on MnSi, Matsunaga et al. [6] reported the presence

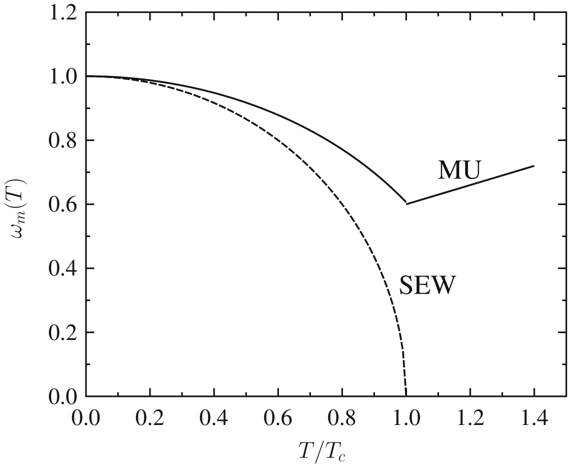

Fig. 6.1 Temperature dependence of the spontaneous volume magneto-striction by the SEW and the MU theories: the difference results from whether the effect of the thermal spin fluctuation amplitude $\xi^2(T)$ is present or not

of these two effects. The same analyses were also reported by Ogawa [7] on $ZrZn_2$, by Suzuki and Masuda [34, 35] on Ni_3Al, and by Shimizu et al. [50] on (Fe,Co)Si.

Stimulated by the MU theory, various theoretical investigations have been made since then. For instance, Hasegawa [8] has treated the magneto-volume effect of Hubbard model in the case with larger amplitudes of spin fluctuations based on the functional integral method by using the static single-site approximation. Results of the temperature dependence of the spontaneous magneto-striction were reported. Volume dependence of the model is included by the $V^{-5/3}$-dependence of d-band width by Heine [5]. The same numerical method was applied on the temperature dependence of the magneto-volume striction by Kakehashi [9] based on the Liberman-Pettifor's Virial theorem. These authors also reported their results of numerical studies on the pressure effect on the Curie temperature [10] the elastic constant of Fe at finite temperature [11] as well as Invar effect [12, 13]. On the other hand, the following result of magnetic pressure,

$$V_0 P_{\rm mag}(T) \simeq \frac{5}{3}[U(T) + Im^2(T)/4], \tag{6.23}$$

was derived by Holden [14] to show that so much drastic change of the volume magneto-striction does not happen above T_c with no spontaneous moment. In (6.23), $U(T)$ and $m(T)$ represent the internal energy and the amplitude of the local magnetic moment, respectively. Along the line of this theory, the magneto-volume effect of Fe–Co alloy is theoretically treated by Joynt [15].

The purpose of most of these theories was to understand the magneto-volume effect associated with electronic band structure of magnetic materials. This book rather sticks to the predominant roles of collective magnetic excitation on various magnetic phenomena. Then Grüneisen's approach to the thermal expansion will be very helpful. We are also required to cope with the following questions.

- What is the origin of the magneto-volume effect?
  If we insist on the predominant roles of the spin fluctuations, it is better to deal with the magneto-volume effect based on the same free energy, which is used in our previous discussions on various magnetic and thermal properties. The magneto-volume effect is to be related with the direct volume dependence of the free energy. Originally, the electron gas model was assumed for the dispersion of the conduction electrons in the spin fluctuation theory by Moriya and Kawabata [16, 17]. Based on the same model and approach, the magneto-volume effect was treated later by Edwards and Macdonard [18]. By assuming the volume dependence for the dispersion of the electron gas model, they have derived the volume strain and the pressure effect on the critical temperature T_c. Since only the perpendicular components of fluctuations are included with respect to the induced magnetization, it is inconsistent with the rotational symmetry of the system. Their volume expansion gives the ratio $\eta(T_c) = \omega_m(T_c)/\omega_m(0) > 1$ at $T = T_c$, in disagreement with 3/5 predicted by the MU theory. It may result from the symmetry breaking treatment, according to their arguments.
- Are there any contributions from zero-point spin fluctuation amplitudes?
  The presence of the zero-point amplitude is likely to be neglected from the beginning. The reason to neglect only one out of artificially divided two components is not so clear. Solontsov and Wagner (1995) argued that because of the nonlinear effect of zero-point spin amplitudes, the right hand of (6.22) can be rewritten by [19]
  $$\omega_m(T) = \rho\kappa C M^2 + \rho\kappa \sum_{\nu} [C(\delta m_\nu^2)_T + C_0(\delta m_\nu^2)_Z], \tag{6.24}$$
  where ν denotes the transverse and the longitudinal components with respect to the spontaneous magnetization. The last term represents the contribution from zero-point spin fluctuations. The same origin is assumed for the magneto-volume coupling constants as those of the SEW and MU theories.
- What the relation between the pressure effects on the spontaneous magnetization and the critical temperature is satisfied?
- Is there any relation between the magneto-volume effect and the magnetic specific heat?
  If the same free energy as that for the specific heat is used for the magneto-volume effect, some kind of Grüneisen's relation should be satisfied between them.
- Are there any differences between the spontaneous and forced magneto-striction?

6.3 Volume Dependence of the Free Energy

In our view, the magneto-volume effect should be treated in the same way as the entropy and the specific heat in Chap. 5. It is then better to employ the free energy (5.2) as the magnetic contribution F_m in (6.9) [20]. Let us divide it into two parts, i.e., the thermal and the other components, F_{th} and F_{zp}, respectively.

$$
\begin{aligned}
F_m(y,\sigma,t,\omega) &= F_{th}(y,y_z,\sigma,t,\omega) + F_{zp}(y,y_z,\sigma,t,\omega) \\
F_{th} &= \frac{2}{\pi}\sum_q{}' \int_0^\infty \mathrm{d}\nu\, T\log(1-\mathrm{e}^{-\nu/T})\frac{\Gamma_q}{\nu^2+\Gamma_q^2} \\
&\quad + \frac{1}{\pi}\sum_q \int_0^\infty \mathrm{d}\nu\, T\log(1-\mathrm{e}^{-\nu/T})\frac{\Gamma_q^z}{\nu^2+(\Gamma_q^z)^2} + \Delta F_{th} \qquad (6.25) \\
F_{zp} &= \frac{1}{\pi}\sum_q \int_0^{\nu_c} \mathrm{d}\nu\, \frac{\nu}{2}\left\{2\frac{\Gamma_q}{\nu^2+\Gamma_q^2} + \frac{\Gamma_q^z}{\nu^2+(\Gamma_q^z)^2}\right\} \\
&\quad + N_0T_A y\sigma^2 - \frac{1}{3}N_0T_A\left\langle S_i^2\right\rangle_{\text{tot}}(3y+\Delta y_z) + \Delta F_{zp}
\end{aligned}
$$

The corrections ΔF_{th} and ΔF_{zp} represent the thermal and all the rest components of ΔF_1 in (5.2), respectively. Since the effect of spin waves is neglected here, for simplicity, the summation $\sum{}'$ means that the spin-wave region around the origin is excluded.

Notice that two spectral parameters T_0 and T_A are included in the above free energy. They correspond to the Debye temperature Θ_D in the model of lattice vibrations. It is therefore reasonable to assume that these parameters are volume dependent. On the other hand, variables y, Δy_z, and σ should be determined by the extremum conditions of the free energy as well as to satisfy the thermodynamic relations. In the following, we are particularly concerned with the explicit volume dependence of the free energy. Its explicit volume deviation is then denoted by

$$
\delta_{\mathrm{v}} F_m = \delta_{\mathrm{v}} F_{th} + \delta_{\mathrm{v}} F_{zp}, \quad \delta_{\mathrm{v}} f(y,\sigma,t,\omega) \equiv \frac{\partial f(y,\sigma,t,\omega)}{\partial\omega}\delta\omega. \qquad (6.26)
$$

To begin with, let us first examine how the thermal component of the free energy F_{th} is affected by the volume change of crystals. From the volume dependence of the spectral parameter T_0, the volume change will give rise to following deviation of the damping constant in (6.25):

$$
\delta_{\mathrm{v}}\Gamma_q = 2\pi\delta T_0 x(y+x^2) = \frac{\delta T_0}{T_0}\Gamma_q, \quad \delta_{\mathrm{v}}\Gamma_q^z = \frac{\delta T_0}{T_0}\Gamma_q^z \qquad (6.27)
$$

Consequently, the variation of the thermal component of the free energy is written in the form

$$
\begin{aligned}
\delta_{\mathrm{v}} F_{th} &= \frac{\delta T_0}{T_0}\frac{1}{\pi}\sum_q\int_0^\infty \mathrm{d}\nu T\log(1-\mathrm{e}^{-\nu/T}) \\
&\quad \times\left\{2\Gamma_q\frac{\partial}{\partial\Gamma_q}\left(\frac{\Gamma_q}{\nu^2+\Gamma_q^2}\right) + \Gamma_q^z\frac{\partial}{\partial\Gamma_q^z}\left(\frac{\Gamma_q^z}{\nu^2+(\Gamma_{q^z})^2}\right)\right\} + \delta_{\mathrm{v}}\Delta F_{th} \\
&= \frac{\delta T_0}{T_0}\frac{1}{\pi}\sum_q\int_0^\infty \mathrm{d}\nu n(\nu)\left\{2\frac{\nu\Gamma_q}{\nu^2+\Gamma_q^2} + \frac{\nu\Gamma_q^z}{\nu^2+(\Gamma_q^z)^2}\right\} + \delta_{\mathrm{v}}\Delta F_{th}, \qquad (6.28)
\end{aligned}
$$

by using integration by parts and the following relation:

$$\frac{\partial}{\partial \nu}\frac{\nu}{\nu^2+\Gamma^2} = -\frac{\partial}{\partial \Gamma}\frac{\Gamma}{\nu^2+\Gamma^2}. \tag{6.29}$$

The last line of (6.28) is rewritten by using the derivative of the function $\Phi(u)$ defined in (5.21). The wave-vector summation and the frequency integral is given by

$$\frac{T}{N_0}\sum_q \frac{\Gamma_q}{2\pi T}\cdot 2\int_0^\infty \mathrm{d}\nu \frac{\nu}{\mathrm{e}^{\nu/T}-1}\frac{1}{\nu^2+\Gamma_q^2} = 3T_0 t\int_0^1 \mathrm{d}x x^2 u(x)\Phi'[u(x)],$$

where $x = q/q_B$ is the reduced wave-number and $u(x) = \Gamma_q/2\pi T$. With this result, the first term in (6.28) is further rewritten as

$$\delta_{\mathrm{v}} F_{th} = 3N_0 T_0 \frac{\delta T_0}{T_0} t\left[2\int_{x_c}^1 \mathrm{d}x x^2 u\Phi'(u) + \int_0^1 \mathrm{d}x x^2 u_z \Phi'(u_z)\right] \tag{6.30}$$

where $u = x(y+x^2)/t$ and $u_z = x(y_z+x^2)/t$. The derivative of the thermal component ΔF_{th} with regards to $\Delta y_z \equiv y_z - y$ is given by

$$\delta_{\mathrm{v}}\left(\frac{\partial \Delta F_{th}}{\partial \Delta y_z}\right) = -2N_0\delta_{\mathrm{v}}\{T_0[A(y_z,t)-A(y,t)]\}$$

Let us first evaluate the variation of the right hand side. Then its integral with respect to Δy_z gives

$$\delta_{\mathrm{v}}\Delta F_{th} \simeq -2N_0 T_0\frac{\delta T_0}{T_0}\Delta y_{z0}\left\{A(y_{z0},t) - A(0,t) - t\left[\frac{\partial A(y_{z0},t)}{\partial t} - \frac{\partial A(0,t)}{\partial t}\right]\right\}\delta\omega \tag{6.31}$$

where $y_z = y_{z0}$ and $y = 0$ are assumed since we need the spontaneous striction here.

As for the component F_{zp}, it can be expanded with respect to y and Δy_z around their origins. The deviation $\delta_{\mathrm{v}} F_{zp}$ is then expanded as follows:

$$\delta_{\mathrm{v}} F_{zp}(y,\Delta y_z,\omega) = \delta_{\mathrm{v}} F_{zp}(0,0,\omega) + \frac{\partial \delta_{\mathrm{v}} F_{zp}(0,0,\omega)}{\partial y} y + \frac{\partial \delta_{\mathrm{v}} F_{zp}(0,0,\omega)}{\partial \Delta y_z}\Delta y_z + \cdots. \tag{6.32}$$

To evaluate the above linear coefficients with respect to y and Δy_z, note the relations (5.3), (5.5), and (5.8) in Chap. 5 are satisfied. In (6.32), the derivatives of $F_{zp}(y, y_z, \omega)$ with respect to these variables are then given by

$$
\begin{aligned}
\frac{\partial F_{zp}(y, \Delta y_z, \omega)}{\partial y} &\to N_0 T_A \left[\left\langle \delta S_{\rm loc}^2 \right\rangle_Z (0,0) + \sigma^2 - \left\langle S_{\rm loc}^2 \right\rangle_{\rm tot} \right], \\
\frac{\partial F_{zp}(y, \Delta y_z, \omega)}{\partial \Delta y_z} &\to N_0 T_A \left[\left\langle (\delta S_{\rm loc}^z)^2 \right\rangle_Z (0) - \frac{1}{3} \left\langle S_{\rm loc}^2 \right\rangle_{\rm tot} - \lambda_{zp}(\sigma, t) \right], \\
\lambda_{zp}(\sigma, t) &\to -\frac{\sigma^2}{3}, \quad \text{for } y \to 0 \text{ and } \Delta y_z \to 0,
\end{aligned}
\tag{6.33}
$$

where $\lambda_{zp}(\sigma, t)$ represents a portion of $\lambda(\sigma, t)$ in (5.9) excluding the thermal contributions. By exchanging the order of the variation $\delta_{\rm v}$ and the differentiation with respect to y or Δy_z, the right hand side of (6.32) is rewritten in the form

$$
\begin{aligned}
\frac{\partial \delta_{\rm v} F_{zp}}{\partial y} &= \delta_{\rm v} \left(\frac{\partial F_{zp}}{\partial y} \right) = -N_0 \delta_{\rm v} \left[T_A \Delta \left\langle S_{\rm loc}^2 \right\rangle_{\rm tot} \right] + N_0 \delta T_A \sigma^2 \\
\frac{\partial \delta_{\rm v} F_{zp}}{\partial \Delta y_z} &= \frac{1}{3} \frac{\partial \delta_{\rm v} F_{zp}}{\partial y}, \quad \Delta \left\langle S_{\rm loc}^2 \right\rangle \equiv \left\langle S_{\rm loc}^2 \right\rangle_{\rm tot} - \left\langle S_{\rm loc}^2 \right\rangle_Z (0).
\end{aligned}
\tag{6.34}
$$

After all, the variation of the free energy due to the volume change is given by

$$
\begin{aligned}
&\delta_{\rm v} F_{zp}(y, y_z, \sigma, t, \omega) = -N_0 C_{zp}(2y + y_z)\delta\omega + \cdots, \\
&3C_{zp}\delta\omega = \delta_{\rm v} \left[T_A \Delta \left\langle S_{\rm loc}^2 \right\rangle \right] - \sigma^2 \delta T_A.
\end{aligned}
\tag{6.35}
$$

For ferromagnets, since $\Delta \left\langle S_{\rm loc}^2 \right\rangle$ and $\sigma_0^2(0)$ are of the same order of magnitude, the term $\sigma^2 \delta T_A$ in the above second line cannot be neglected. On the other hand, the first term $\delta_{\rm v} F_{zp}(0, 0, \omega)$ in (6.32) is neglected, for it is constant independent of temperature.

With these free energy variations given in (6.30) and (6.35), the volume magnetostriction is evaluated by their derivatives with respect to the volume stain ω, i.e., as the sum of two components,

$$
\begin{aligned}
\omega_m(t) &= -\frac{\kappa}{V} \frac{\partial F_m}{\partial \omega} = \omega_{th}(t) + \omega_{zp}(t), \\
\omega_{th}(t) &= -\frac{\kappa}{V} \frac{\partial F_{th}}{\partial \omega}, \quad \omega_{zp}(t) = -\frac{\kappa}{V} \frac{\partial F_{zp}}{\partial \omega}.
\end{aligned}
\tag{6.36}
$$

6.3.1 Magnetic Grüneisen Parameters

Let us next introduce magnetic Grüneisen parameters in place of magneto-volume coupling constants. If we note the expression of the variations of free energies (6.28) and (6.32), it will be appropriate to define the following three Grüneisen parameters [20].

- Two parameters, γ_0 and γ_A, that characterize the volume dependence of spectral parameters T_0 and T_A.
  These spectral parameters are defined as distribution widths of the imaginary part of the dynamical magnetic susceptibility $\mathrm{Im}\chi(q,\omega)$ in frequency and wave-vector spaces, respectively. They therefore correspond to the Debye temperature Θ_D in lattice vibrations and the exchange interaction constant J in the Heisenberg model of localized spin systems. The following two magnetic Grüneisen parameters are defined as strain derivatives of logarithm of these values.

$$\gamma_0 = -\frac{\mathrm{d}\log T_0}{\mathrm{d}\omega}, \quad \gamma_A = -\frac{\mathrm{d}\log T_A}{\mathrm{d}\omega}, \tag{6.37}$$

  In terms of these parameters, variations of δT_0 and δT_A are represented by

$$\frac{\delta T_0}{T_0} = \frac{\mathrm{d}\log T_0}{\mathrm{d}\omega}\delta\omega = -\gamma_0\delta\omega, \quad \frac{\delta T_A}{T_A} = -\gamma_A\delta\omega.$$

- Parameter γ_m that characterize the volume dependence of the spin fluctuation amplitude, $\Delta\left\langle S_{\mathrm{loc}}^2\right\rangle$ defined in (6.34).
  This difference of the amplitudes is supposed to depend on the volume of the system. From the strain derivative of its logarithm, the third Grüneisen parameter is defined by

$$\gamma_m = \frac{\mathrm{d}\log\Delta\left\langle S_{\mathrm{loc}}^2\right\rangle}{\mathrm{d}\omega}. \tag{6.38}$$

  Because of the spin amplitude conservation, the value $\Delta\left\langle S_{\mathrm{loc}}^2\right\rangle$ is equivalent to the critical thermal amplitude squared $\left\langle S_{\mathrm{loc}}^2\right\rangle_T(0,t_c)$, i.e., the value $3\sigma_0^2(0)/5$ according to (3.12) in Chap. 3. Thus the above definition is also written in the form

$$\frac{\mathrm{d}\Delta\left\langle S_{\mathrm{loc}}^2\right\rangle}{\mathrm{d}\omega} = \frac{3}{5}\sigma_0^2(0)\gamma_m. \tag{6.39}$$

With these definitions, the coefficient C_{zp} in (6.35) is given by

$$\begin{aligned} C_{zp} &= \frac{1}{3}T_A\left\{\frac{\mathrm{d}\log T_A}{\mathrm{d}\omega}\left[\langle S_{\mathrm{loc}}^2\rangle - \sigma^2\right] + \frac{\mathrm{d}\log\Delta\langle S_{\mathrm{loc}}^2\rangle}{\mathrm{d}\omega}\Delta\langle S_{\mathrm{loc}}^2\rangle\right\} \\ &= \frac{1}{5}T_A\sigma_0^2(0)\left[\gamma_m + \gamma_A\left(\frac{5}{3}\frac{\sigma^2}{\sigma_0^2(0)} - 1\right)\right]. \end{aligned} \tag{6.40}$$

For later convenience, let us also introduce the following ratios g_A and g_0 defined by

$$g_A = \frac{\gamma_A}{\gamma_m}, \quad g_0 = \frac{\gamma_0}{\gamma_m} \tag{6.41}$$

According to Fawcett [21], Grüneisen parameters are defined as negatives of volume-strain derivatives of the logarithm of characteristic energy scales of phenomena. The first two parameters are introduced according to this criterion. It represents the variation of the spectral widths caused by the volume contraction by external pressure. They are equivalent of the volume dependence, $T_0 \propto V^{-\gamma_0} \propto e^{-\gamma_0 \omega}$, $T_A \propto V^{-\gamma_A} \propto e^{-\gamma_A \omega}$. For the analysis of thermal expansion of heavy fermion systems, the Grüneisen parameter is introduced into the SCR spin fluctuation theory by Kambe et al. [22]. However, the volume dependence of parameter T_0 and T_A was assumed to be neglected.

6.3.2 Forced Magneto-Striction and Maxwell Relation

In our treatment of the magnetic specific heat in Chap. 5, we show that the Maxwell relation is satisfied for our free energy, i.e., (5.58) and (5.65) in the paramagnetic and ordered phases, respectively. Since the same free energy is used in this chapter, we assume from the beginning that the relation is satisfied.

For the free energy with independent variables σ and pressure p, its total derivative is given by

$$\mathrm{d}F(\sigma, p) = V\mathrm{d}p + N_0 h \mathrm{d}\sigma. \tag{6.42}$$

The following Maxwell relation is then satisfied.

$$\frac{1}{V}\frac{\partial V}{\partial \sigma}\bigg|_p = \frac{\partial \log V}{\partial \sigma}\bigg|_p = \frac{\partial \omega}{\partial \sigma}\bigg|_p = \frac{N_0}{V}\frac{\partial h}{\partial p}\bigg|_\sigma. \tag{6.43}$$

With the use of the compressibility κ, the pressure derivative is replaced by the ω derivative by

$$\frac{\partial}{\partial p} = -\kappa\frac{\partial}{\partial \omega}, \quad \kappa \equiv -\frac{\partial \omega}{\partial p}\bigg|_\sigma. \tag{6.44}$$

The relation in (6.43) is therefore written in the form

$$\frac{\partial \omega(\sigma, t)}{\partial \sigma} = \frac{N_0}{V}\sigma\frac{\partial(2T_A y)}{\partial p} = -2\kappa\rho\sigma\frac{\partial(T_A y)}{\partial \omega}, \tag{6.45}$$

where $\rho = N_0/V$ and $y = h/2T_A\sigma$. After substituting the Grüneisen parameter γ_A into the volume dependence of T_A, (6.45) is finally given by

$$\begin{aligned}
&\frac{\partial \omega_h(\sigma, t)}{\partial \sigma} = 2\rho\kappa C_h(\sigma, t)\sigma, \\
&C_h(\sigma, t) = -T_A\left(\frac{1}{T_A}\frac{\partial T_A}{\partial \omega}y + \frac{\partial y}{\partial \omega}\right) = T_A\left[\gamma_A y(\sigma, t) - \frac{\partial y(\sigma, t)}{\partial \omega}\right].
\end{aligned} \tag{6.46}$$

Hereafter, the forced magneto-striction is denoted by $\omega_h(\sigma, t)$ to avoid confusion.

Equation (6.46) is regarded as the general expression for the forced magneto-striction. To evaluate the value of $\omega_h(\sigma, t)$ at arbitrary value of σ, we need to find the solution of (6.46) by regarding its first line as a differential equation in σ. Because of the σ dependence of the coupling constant $C_h(\sigma, t)$, we have to know the σ dependence of $y(\sigma, t)$ and its volume derivative $\partial y(\sigma, t)/\partial\omega$.

6.4 Volume Magneto-Striction for Ferromagnets

Spontaneous and forced magneto-strictions are treated in this section based on the volume dependence of the free energy in Sect. 6.3. Let us first deal with systems of ferromagnets.

6.4.1 Magneto-Volume Effect in the Ground State

In the ground state with no thermal spin fluctuation amplitudes, inverses of reduced magnetic susceptibilities are given by $y(\sigma_0, 0) = 0$ and $y_z(\sigma_0, 0) = y_{z0}(0) = 2y_1(0)\sigma_0^2(0)$. The spontaneous magnetic moment is denoted by $\sigma_0(0)$. In this case, the spontaneous and forced magneto-strictions, $\omega_{zp}(0)$ and $\omega_h(\sigma, 0)$, are evaluated as follows.

- Spontaneous magneto-striction
  Since $\sigma = \sigma_0(0)$ is satisfied in (6.40) in the absence of the external field, $C_{zp}(0)$ is given by

$$C_{zp}(0) = \frac{1}{5}\left(\gamma_m + \frac{2}{3}\gamma_A\right) T_A \sigma_0^2(0). \tag{6.47}$$

  From (6.35) and (6.36), the spontaneous magneto-striction is given by

$$\begin{aligned} &\omega_{zp}(0) = \rho\kappa C_{zp}(0) y_{z0}(0) = \rho\kappa C_s(0)\sigma_0^2(0), \quad y_{z0}(0) = 2y_1(0)\sigma_0^2(0), \\ &C_s(0) = 2C_{zp}(0)y_1(0) = \frac{2}{5}\left(\gamma_m + \tfrac{2}{3}\gamma_A\right) T_A y_1(0)\sigma_0^2(0). \end{aligned} \tag{6.48}$$

  The function $C_s(0)$ has a meaning of the magneto-volume coupling constant for the spontaneous striction.
- Forced magneto-striction
  In the region of weak external magnetic field, the σ dependence of $C_h(\sigma, t)$ in (6.46) is neglected. The forced striction is given by

$$\omega_h(\sigma, t) = \rho\kappa C_h(\sigma_0, 0)[\sigma^2 - \sigma_0^2(0)]. \tag{6.49}$$

The magneto-volume coupling constant $C_h(\sigma_0, 0)$ is also evaluated by putting the σ dependence of $y(\sigma, t) \simeq y_1(0)[\sigma^2 - \sigma_0^2(0)]$ into (6.46).

$$\begin{aligned} C_h(\sigma_0, 0) &= -T_A \frac{\partial}{\partial\omega}\{y_1(0)[\sigma^2 - \sigma_0^2(0)]\}\Big|_{\sigma=\sigma_0} \\ &= -T_A \left\{ \frac{\partial y_1(0)}{\partial\omega}[\sigma^2 - \sigma_0^2(0)] - y_1(0)\frac{\partial\sigma_0^2(0)}{\partial\omega} \right\}\Big|_{\sigma=\sigma_0} \\ &= T_A y_1(0)\gamma_m \sigma_0^2(0). \end{aligned} \tag{6.50}$$

Thus it depends only on the parameter γ_m in the ground state.
If we define $C_h(t) \equiv C_h(\sigma_0, 0)$, the comparison of two magneto-volume coupling constants, (6.48) and (6.50), for spontaneous and forced strictions leads to the relation:

$$\frac{C_s(0)}{C_h(0)} = \frac{2}{5}\left(1 + \frac{2}{3}g_A\right), \tag{6.51}$$

where g_A is defined in (6.41). The quite different result is derived from $C_s = C_h$ by the SEW and the MU theories.

- Effect of pressure on spontaneous magnetic moment
  From the definition of γ_m, the ω derivative of $\sigma_0^2(0, \omega)$ is given by

$$\frac{1}{\Delta\langle S_{\text{loc}}^2\rangle}\frac{\mathrm{d}\Delta\langle S_{\text{loc}}^2\rangle}{\mathrm{d}\omega} = \frac{1}{\sigma_0^2(0)}\frac{\mathrm{d}\sigma_0^2(0)}{\mathrm{d}\omega} = \gamma_m. \tag{6.52}$$

  It follows that the pressure dependence of the spontaneous moment is given by

$$\sigma_0^2(0, \omega) = \sigma_0^2(0, 0)(1 + \gamma_m\omega) = \sigma_0^2(0)(1 - \kappa\gamma_m p). \tag{6.53}$$

  The parameter γ_m can be therefore estimated by the change of the spontaneous magnetization at low temperatures induced by external pressure.

In conclusion, the magneto-volume effect in the ground state is described by

$$\omega_m(M, 0) = \frac{\rho\kappa C_s(0)}{(2N_0\mu_{\text{B}})^2}M_0^2(0) + \frac{\rho\kappa C_h(0)}{(2N_0\mu_{\text{B}})^2}[M^2 - M_0^2(0)], \tag{6.54}$$

with two different coupling constants.

6.4.2 Ferromagnets at Finite Temperatures

Temperature dependence of thermal volume expansion Spontaneous magneto-striction in the ordered phase is also obtained according to the general expression of the volume striction (6.36). It consists of two components, $\omega_{th}(t)$ in (6.30) and $\omega_{zp}(t)$ in (6.35), derived by the volume derivatives of corresponding components of the free energy. They are given by

$$\begin{aligned}
\omega_{th}(t) &= 3\rho\kappa T_0\gamma_0 t\left[2\int_{x_c}^{1}\mathrm{d}x x^2 u\Phi'(u) + \int_0^1 \mathrm{d}x x^2 u_z\Phi'(u_z)\right] + \Delta\omega_{th}(t), \\
\omega_{zp}(t) &= \rho\kappa C_{zp}(t)y_{z0}(t) = \rho\kappa C_s(t)\sigma_0^2(t), \quad y_{z0}(t) = 2y_1(t)\sigma_0^2(t), \\
C_s(t) &= \frac{2}{5}C_h(0)\frac{V(t)}{U(t)}\left[1 + g_A\left(\frac{5}{3}U(t) - 1\right)\right], \quad \frac{y_1(t)}{y_1(0)} = \frac{V(t)}{U(t)},
\end{aligned} \tag{6.55}$$

where $U(t)$ and $V(t)$ are defined in (4.21). The coefficient $C_{zp}(t)$ defined in (6.40) is given by

$$C_{zp}(t) = \frac{1}{5}T_A\sigma_0^2(0)\left[\gamma_m + \gamma_A\left(\frac{5}{3}U(t) - 1\right)\right], \tag{6.56}$$

for $\sigma = \sigma_0(t)$ in the absence of external field at finite temperatures. In the same way, the thermal expansion derived from the free energy correction ΔF_{th} is given by

$$\Delta\omega_{th}(t) = 2\rho\kappa T_0\gamma_0\Delta y_{z0}\left\{t\left[\frac{\partial A(y_{z0},t)}{\partial t} - \frac{\partial A(0,t)}{\partial t}\right] - A(y_{z0},t) + A(0,t)\right\}. \tag{6.57}$$

Thermal component $\omega_{th}(t)$ in (6.55) results from the thermal component of the free energy. It therefore increases monotonically with increasing temperature. In the paramagnetic phase, $u = u_z$ and $y = y_z$ are satisfied, as well as $x_c = 0$ since no spin-waves are present. The thermal correction $\Delta\omega_{th}(t)$ is also absent. The component $\omega_{zp}(t)$ from zero-point fluctuations is proportional to $\sigma_0^2(t)$, in the ordered phase. In the paramagnetic phase, it becomes proportional to the inverse of the magnetic susceptibility $y_0(t)$, since $3y_0(t)$ appears in place of $y_{z0}(t)$ for $T < T_c$. Its temperature dependence is similar to that of the MU theory. Using the correspondence between $y_0(t)$ and $y_1(t)\sigma_0^2(t)$ in the paramagnetic and the ordered phases, the definition (4.21) can be extended to the paramagnetic phase by

$$U(t) = \frac{y_0(t)}{y_1(t)\sigma_0^2(0)}, \quad V(t) = \frac{y_0(t)}{y_1(0)\sigma_0^2(0)} = \frac{y_1(t)}{y_1(0)}U(t). \tag{6.58}$$

In the paramagnetic phase, the temperature dependence of $\omega_{zp}(t)$ is then written by

$$\begin{aligned}
\omega_{zp}(t) &= \rho\kappa C_{zp}(t)[3y_0(t)] = \rho\kappa C_s(t)\frac{y_0(t)}{y_1(t)}, \\
C_{zp}(t) &= \frac{1}{5}T_A\sigma_0^2(0)(\gamma_m - \gamma_A), \quad C_s(t) \equiv 3y_1(t)C_{zp}(t)
\end{aligned} \tag{6.59}$$

In terms of reduced parameters, (6.59) is finally represented by

$$\begin{aligned}\omega_{zp}(t) &= \rho\kappa C_s(t)\sigma_0^2(0)U(t)\\ C_s(t) &= \frac{3}{5}C_h(0)(1-g_A)\frac{y_1(t)}{y_1(0)} = \frac{3}{5}C_h(0)(1-g_A)\frac{V(t)}{U(t)}.\end{aligned} \tag{6.60}$$

Hereafter, let us introduce the constant ω_0 by

$$\omega_0 = \rho\kappa C_h(0)\sigma_0^2(0), \tag{6.61}$$

as a unit of volume-strain. The component $\omega_{zp}(t)$ in (6.59) is then given in more simplified form

$$\omega_{zp}(t) = \frac{3}{5}\omega_0(1-g_A)V(t). \tag{6.62}$$

The ratios of each component of thermal expansions in (6.55) to the unit strain ω_0 are also written by

$$\begin{aligned}\frac{\omega_{th}(t)}{\omega_0} &= \frac{g_0 t}{5c[y_1(0)\sigma_0^2(0)]^2}\\ &\quad\times\left\{2\int_{x_c}^1 \mathrm{d}x x^2 u\Phi'(u) + \int_0^1 \mathrm{d}x x^2 u_z\Phi'(u_z)\right\} + \frac{\Delta\omega_{th}(t)}{\omega_0},\\ \frac{\Delta\omega_{th}(t)}{\omega_0} &= \frac{2g_0 y_{z0}}{15c[y_1(0)\sigma_0^2(0)]^2}\\ &\quad\times\left\{t\left[\frac{\partial A(y_{z0},t)}{\partial t} - \frac{\partial A(0,t)}{\partial t}\right] - A(y_{z0},t) + A(0,t)\right\},\\ \frac{\omega_{zp}(t)}{\omega_0} &= \frac{2}{5}V(t)\left[1 + g_A\left(\frac{5}{3}U(t) - 1\right)\right].\end{aligned} \tag{6.63}$$

Likewise, thermal expansion coefficients are also given as the sum of reduced components:

$$\begin{aligned}\beta(t) &= \frac{\mathrm{d}\omega_s(t)}{\mathrm{d}T} = \frac{\omega_0}{T_0}\bar{\beta}(t),\\ \bar{\beta}(t) &= \frac{\mathrm{d}\omega_s(t)}{\mathrm{d}t} = \bar{\beta}_{th}(t) + \Delta\bar{\beta}_{th}(t) + \bar{\beta}_{zp}(t).\end{aligned} \tag{6.64}$$

Each of them are given by

$$\begin{aligned}\bar{\beta}_{th}(t) = \frac{cg_0}{5A^2(0,t_c)}\Bigg\{&-2\int_{x_c}^1 \mathrm{d}x x^2 u^2\Phi''(u) - \int_0^1 \mathrm{d}x x^2 u_z^2\Phi''(u_z)\\ &+ \frac{\mathrm{d}V(t)}{\mathrm{d}t}\Bigg[-\frac{tx_c}{V(t)}x_c^2 u_c\left(\log u_c - \frac{1}{2u_c} - \psi(u_c)\right)\\ &+ 2y_1(0)\sigma_0^2(0)\left(A(y_{z0},t) - t\frac{\partial A(y_{z0},t)}{\partial t}\right)\Bigg]\Bigg\},\end{aligned}$$

$$\Delta\bar{\beta}_t(t) = \frac{4g_0}{15A(0,t_c)}\left\{V'(t)\left[t\left(\frac{\partial A(y_{z0},t)}{\partial t} - \frac{\partial A(0,t)}{\partial t} + y_{z0}\frac{\partial A'(y_{z0},t)}{\partial t}\right)\right.\right. \tag{6.65}$$

$$\left.- A(y_{z0},t) + A(0,t) - y_{z0}A'(y_{z0},t)\right]$$

$$\left.+ tV(t)\left[\frac{\partial^2 A(y_{z0},t)}{\partial t^2} - \frac{\partial^2 A(0,t)}{\partial t^2}\right]\right\},$$

$$\bar{\beta}_{zp}(t) = \frac{2}{5}\left\{(1-g_A)V'(t) + \frac{5}{3}g_A[V'(t)U(t) + V(t)U'(t)]\right\}, \quad u_c = x_c^3/t,$$

where $A'(y,t) \equiv \partial A(y,t)/\partial y$.

These results derived above are different from those of the MU theory in the following respects.

1. The presence of an extra thermal volume expansion, $\omega_{th}(t)$, in (6.55).
   Its temperature dependence is quite different from the one derived by Moriya and Usami, although both are associated with thermal spin fluctuation amplitudes.
2. The magneto-volume coupling constants do depend on temperature.
   The reason is because Grüneisen parameters are not defined as the expansion coefficient with respect to $\sigma_0^2(t)$, but $\Delta y_z = y_{z0}(t)$. Hence, there appears in $C_s(t)$ the temperature dependent proportionality factor $y_1(t)$ contained in $y_{z0}(t)$. In addition for finite γ_A, another dependence proportional to $\sigma_0^2(t)$ also appears. At the critical point, it vanishes, i.e., $C_s(t_c) = 0$, reflecting the temperature dependence of $y_1(t)$.
   The dependence of $C_h(t)$ for the forced magneto-striction will be explained later.
3. Spontaneous and forced magneto-volume coupling constants, C_s and C_h, are different in their magnitudes.

Volume Expansion below T_c The ratio of spontaneous magneto-volume strictions at $T = 0$ and $T = T_c$, i.e., $\eta = \omega_m(t_c)/\omega_m(0)$, was introduced by the MU theory, as a measure of the volume contraction from the ground state to the critical point with increasing temperature. They claimed that the value of η is different for the SEW and MU theories. Because the magneto-volume coupling constants are different for the spontaneous and the forced magneto-strictions in our theory, the same comparison is impossible. Therefore, it seems rather preferable to introduce a new definition of η by

$$1-\eta = \frac{\Delta\omega_m(0)}{\omega_0}, \quad \Delta\omega_m(t) = \omega_m(t) - \omega_m(t_c). \tag{6.66}$$

In place of $\omega_m(0)$ in the denominator, we employ our unit strain ω_0 defined in (6.61) evaluated by using the forced magneto-volume coupling constant $C_h(0)$.

In the SEW theory with no thermal amplitudes at the critical point, $1-\eta = 1$ (i.e., $\eta = 0$) is derived, for $\omega_m(t_c) = 0$ is satisfied. According to the MU theory, on the other hand, η is given by

$$1-\eta = \frac{1}{\omega_0(0)}[\omega_m(0) - \omega_m(t_c)] = \frac{\sigma_0^2(0) - \xi^2(t_c)}{\sigma_0^2(0)} = \frac{2}{5}, \tag{6.67}$$

for $\omega_m(0) = \omega_0$ and $\xi^2(t_c) = 3\sigma_0^2(0)/5$ are satisfied. The same ratio of η is derived for each of the SEW and the MU theories independent of definitions. The difference between them originates only from the presence of the thermal amplitude $\xi^2(T)$ in (6.22). Whereas in our treatment, the value of $\Delta\omega_m(0)$ is estimated by

$$\begin{aligned}\Delta\omega_m(0) &= [\omega_{th}(0) + \omega_{zp}(0)] - [\omega_{th}(t_c) + \omega_{zp}(t_c)] \\ &= -\omega_{th}(t_c) + \rho\kappa C_s(0)\sigma_0^2(0) = \frac{2}{5}\left(1 + \frac{2}{3}g_A\right)\omega_0 - \omega_{th}(t_c),\end{aligned} \tag{6.68}$$

since $\omega_{th}(0) = 0$ and $\omega_{zp}(t_c) = 0$. The value of $1 - \eta$ is given by

$$1-\eta = \frac{\Delta\omega_m(0)}{\omega_0} = \frac{2}{5}\left(1 + \frac{2}{3}g_A\right) - \frac{\omega_{th}(t_c)}{\omega_0}. \tag{6.69}$$

Nearly the same value as the MU theory is therefore derived, as long as the thermal component $\omega_{th}(t_c)$ is negligible. However, it results from the different origin, i.e., from the different magneto-volume coupling constants, $C_s(0)/C_h(0) \simeq 2/5$. Since the effect of thermal amplitudes is generally involved in (6.69), the value of $1 - \eta$ is not restricted to the single value $2/5$ but will take a variety of values.

Forced Magneto-Striction To estimate the forced magneto-striction for an arbitrary magnetization σ, numerical integration of (6.46) with respect to σ is necessary. Then $\omega_h(\sigma, t)$ is given by

$$\omega_h(\sigma, t) = 2\rho\kappa T_A \int_{\sigma_0(t)}^{\sigma} d\sigma'\sigma' \left[\gamma_A y(\sigma', t) - \frac{\partial y(\sigma', t)}{\partial \omega}\right], \tag{6.70}$$

where $\sigma_0(t) = 0$ in the paramagnetic phase. The derivative $\partial y(\sigma, t)/\partial\omega$ in the above integrand is estimated as a solution of the following simultaneous differential equation:

$$2A(y, t) + A(y_z, t) - c(2y + y_z) + 5cy_1(0)\sigma^2 = 3A(0, t_c), \tag{6.71}$$

$$\begin{aligned}&2[A'(y, t) - c_z]\frac{\partial y}{\partial\omega} + [A'(y_z, t) - c_z]\left[\frac{\partial y}{\partial\omega} + \sigma\frac{\partial}{\partial\sigma}\left(\frac{\partial y}{\partial\omega}\right)\right] \\ &\quad + 5cy_1(0)(-\gamma_A + \gamma_0)\sigma^2 = 3A(0, t_c)\gamma_m(1 - g_A + g_0).\end{aligned} \tag{6.72}$$

Equation (6.71) represents the TAC condition (3.3). The second Eq. (6.72) is its partial derivative with respect to ω. The following relation, derived from $A(0, t_c) = cy_1(0)\sigma_0^2$ in (3.11) and $y_1(0) = T_A/15cT_0$ in (3.10), is used in the above derivation.

$$\frac{\partial \log A(0,t_c)}{\partial \omega} = \frac{\partial \log y_1(0)}{\partial \omega} + \frac{\partial \log \sigma_0^2(0)}{\partial \omega},$$
$$\therefore \frac{\partial A(0,t_c)}{\partial \omega} = (\gamma_m - \gamma_A + \gamma_0)A(0,t_c). \quad (6.73)$$

Equation (6.70) is also written in the form of the derivative with respect to ω as given by

$$\frac{\partial}{\partial \sigma}\left(\frac{\omega_h(\sigma,t)}{\omega_0}\right) = \frac{2c\sigma}{A(0,t_c)}\left[g_A y(\sigma,t) - \frac{1}{\gamma_m}\frac{\partial y(\sigma,t)}{\partial \omega}\right]. \quad (6.74)$$

The forced magneto-striction $\omega_h(\sigma,t)$ is then obtained as the solution of the simultaneous differential equation consisting of (6.71), (6.72), and (6.74).

Initial value of $y(\sigma,t)$ is given by $y_0(t)$ for $\sigma = 0$ in the paramagnetic phase, and 0 for $\sigma = \sigma_0(t)$ in the ordered phase. Initial value of the derivative $\partial y(\sigma,t)/\partial\omega$ in (6.72) and (6.74) is related to the forced magneto-striction in the weak external magnetic field limit. In this limit, (6.46) in the paramagnetic phase is written as

$$\omega_h(\sigma,t) = \rho\kappa C_h(0,t)\sigma^2, \quad C_h(0,t) = T_A y_0(t)\left[\gamma_A - \frac{\partial \log y_0(t)}{\partial \omega}\right], \quad (6.75)$$

for $y(\sigma,t) \simeq y_0(t) + y_1(t)\sigma^2 \to y_0(t)$ in (5.50) is satisfied. The temperature dependence of $y_0(t)$ is determined as the solution of (3.30). Its ω derivative is then given by

$$\left[A'(y_0,t) - c\right]\frac{\partial y_0(t)}{\partial \omega} = \frac{\partial A(0,t_c)}{\partial \omega} = c(\gamma_m - \gamma_A + \gamma_0)y_1(0)\sigma_0(0). \quad (6.76)$$

Thus the initial condition of the derivative $\partial y(\sigma,t)/\partial\omega \to \partial y_0(t)/\partial\omega$ (for $\sigma \to 0$) is estimated by

$$\frac{\partial y_0(t)}{\partial \omega} = -\frac{y_1(t)}{c y_1(0)}\frac{\partial A(0,t_c)}{\partial \omega} = -(\gamma_m - \gamma_A + \gamma_0)\frac{\sigma_0^2(0)}{\sigma_0^2(t)}y_0(t),$$
$$\therefore \frac{\partial \log y_0(t)}{\partial \omega} = -\frac{1}{U(t)}\gamma_m(1 - g_A + g_0), \quad (6.77)$$

with using (3.50) for $y_1(t)$. By putting these results of initial conditions into (6.75), the temperature dependence of $C_h(t)$ is given by

$$C_h(t) \equiv C_h(0,t) = T_A y_1(t)\sigma_0^2(t)\gamma_m\left[g_A + (1 - g_A + g_0)\frac{1}{U(t)}\right],$$
$$\frac{C_h(t)}{C_h(0)} = \frac{V(t)}{U(t)}\left\{1 - g_A[1 - U(t)] + g_0\right\}, \quad (6.78)$$

with the use of $C_h(0)$ defined in (6.50).

In the case of the ordered phase, the initial condition of the derivative is given by

$$\frac{\partial y(\sigma,t)}{\partial\omega} = -y_1(t)\frac{\partial\sigma_0^2(t)}{\partial\omega}, \quad \text{for } \sigma\to\sigma_0(t),$$
$$\frac{\partial\log\sigma_0^2(t)}{\partial\omega} = \frac{\partial\log\sigma_0^2(0)}{\partial\omega} + \frac{\partial\log U(t)}{\partial\omega} = \gamma_m + \frac{\partial\log U(t)}{\partial\omega}, \tag{6.79}$$

since $y(\sigma,t)\simeq y_1(t)[\sigma^2-\sigma_0^2(t)]\to 0$ is satisfied. Equation (6.46) is therefore given by

$$\omega_h(\sigma,t) = \rho\kappa C_h(\sigma_0(t),t)[\sigma^2-\sigma_0^2(t)],$$
$$\frac{C_h(t)}{C_h(0)} = \frac{C_h(\sigma_0(t),t)}{T_A\gamma_m y_1(0)\sigma_0^2(0)} = \frac{1}{\gamma_m}V(t)\frac{\partial\log\sigma_0^2(t)}{\partial\omega} \tag{6.80}$$
$$= \frac{V(t)}{U(t)}\left[U(t)+\frac{1}{\gamma_m}\frac{\partial U(t)}{\partial\omega}\right].$$

To evaluate the initial value of the σ derivative of $\partial y/\partial\omega$ in (6.72), notice the following expression satisfied in the weak field limit:

$$\frac{\partial y(\sigma,t)}{\partial\sigma} = 2y_1(t)\sigma = 2\sigma y_1(0)\frac{V(t)}{U(t)}. \tag{6.81}$$

By exchanging the order of differentiation, its initial value is evaluated by

$$\left.\frac{\partial}{\partial\sigma}\frac{\partial y}{\partial\omega}\right|_{\sigma=\sigma_0(t)} = 2\sigma_0(t)y_1(0)\frac{V(t)}{U(t)}\frac{\partial\log[y_1(0)V(t)/U(t)]}{\partial\omega}$$
$$= 2y_1(0)\sigma_0(0)\frac{V(t)}{\sqrt{U(t)}}\left[-\gamma_A+\gamma_0+\frac{1}{V(t)}\frac{\partial V}{\partial\omega}-\frac{1}{U(t)}\frac{\partial U}{\partial\omega}\right], \tag{6.82}$$

where $y_1(0)\propto T_A/T_0$. In the ordered phase, we need to know the derivatives, $\partial U(t)/\partial\omega$ and $\partial V(t)/\partial\omega$ in (6.79) and (6.82). These values are evaluated by solving the simultaneous differential equations for variables $U(t)$ and $V(t)$ in Chap. 4 and their ω derivatives.

6.5 Magneto-Volume Effect in Some Temperature Ranges

According to our general expressions of the spontaneous and forced magneto-strictions, we show in this section how the effects are described in more detail at low temperatures, around the critical temperature, and at higher temperatures in the paramagnetic phase.

6.5.1 Magneto-Volume Effect at Low Temperature and Grüneisen Relation

At low temperatures where $t \ll 1$ and $y_{z0}(0) \ll 1$ are satisfied, thermal components of the thermal expansion and its temperature coefficient show the following t^2-linear and t-linear dependences, respectively:

$$\begin{aligned}\omega_{th}(t) &\simeq \frac{1}{8}T_0\rho\kappa\gamma_0\{2\log(1/x_c^2) + \log[1/y_{z0}(0)]\}t^2 \\ &\simeq \frac{3}{4}T_0\rho\kappa\gamma_0 t^2\log[1/\sigma_0(0)], \\ \beta_{th}(t) &\simeq \frac{3}{2}\rho\kappa\gamma_0 t\log[1/\sigma_0(0)],\end{aligned} \tag{6.83}$$

where both x_c^2 and $y_{z0}(0)$ are proportional to $\sigma_0^2(0)$. As was already shown in Chap. 5, the magnetic specific heat (5.44) at low temperatures is given by

$$\frac{C_{m0}(t)}{V} \simeq \frac{3}{2}\frac{N_0}{V}t\log[1/\sigma_0(0)] = \frac{3}{2}\rho t\log[1/\sigma_0(0)]. \tag{6.84}$$

It corresponds to the T^2-linear dependence of the free energy:

$$F_m(T) = F_m(0) - \frac{3}{4}N_0\frac{T^2}{T_0}\log[1/\sigma_0(0)] + \cdots, \tag{6.85}$$

for its temperature derivative gives the specific heat in (6.84). The thermal expansion (6.83) is given by the derivative of the above free energy with respect to the strain ω.

$$\omega_{th}(t) = -\frac{\kappa}{V}\frac{\partial F_m(t)}{\partial\omega} = \frac{3}{4}\rho\kappa\gamma_0 t^2\log[1/\sigma_0(0)].$$

From the comparison of (6.83) and (6.84), the following Grüneisen relation between the magnetic specific heat and the thermal volume expansion coefficient is thus satisfied at low temperatures.

$$\beta_{th}(t) = \kappa\gamma_0\frac{C_{m0}(t)}{V} = \frac{3}{2}\rho\kappa\gamma_0 t\log\frac{1}{\sigma_0(0)}. \tag{6.86}$$

The component $\omega_{zp}(t)$ shows similar behavior to those of the SEW theory and the MU theory. It is given in this limit by (6.55), i.e.,

$$\omega_{zp}(t) = \rho\kappa C_s(t)\sigma_0^2(t), \quad \frac{C_s(t)}{C_h(0)} = \frac{2V(t)}{5U(t)}\left[1 + g_A\left(\frac{5}{3}U(t) - 1\right)\right]. \tag{6.87}$$

After substituting the results (4.24) and (4.26) for $V(t)/U(t)$ and $U(t)$ in the above constant $C_s(t)$, we obtain the following temperature dependence.

$$C_s(t) = C_s(0)\left\{1 - \frac{ct^2}{120A^2(0,t_c)} \times \left[\frac{3+2r^2}{4} + \frac{5g_A}{3+2g_A}\frac{4+5r+r^2}{3}\right] + \cdots\right\}, \tag{6.88}$$

where $r = (\pi/2)^2$.

As the sum of these two contributions, the temperature dependence of the spontaneous volume-striction at low temperatures is finally given by

$$\begin{aligned}\frac{\omega_m(t)}{\omega_0} &= \frac{cg_0}{120A^2(0,t_c)}\left[2\log x_c^{-2} + \log y_{z0}^{-1}\right]t^2 + \frac{cg_0(1-r^2)}{180A^2(0,t_c)}t^2 \\ &+ \frac{2}{5}\left(1+\frac{2}{3}g_A\right)\left\{1 - \frac{c\,t^2}{120A^2(0,t_c)} \times \left(\frac{3+2r^2}{4} + \frac{3+7g_A}{3+2g_A}\frac{4+5r+r^2}{3}\right) + \cdots\right\},\end{aligned} \tag{6.89}$$

where the second term in the right hand side results from the thermal free energy correction ΔF_{th}. Because of the above second and the third terms, the t^2-linear coefficient usually becomes negative. The volume change from this origin shows contraction with increasing temperature. For weak itinerant ferromagnets with tiny spontaneous magnetization ($\sigma_0(0) \ll 1$), the positive first term will be also non-negligible. The presence of this $\log[1/\sigma_0(0)]$-linear term is, however, not yet verified experimentally.

Thermal expansion measurements on Ni_3Al and Ni-Pt alloys at low temperatures was made by Kortekaas et al. [23] over the composition ranging from the paramagnets close to the magnetic instability and to the weak ferromagnets. According to their report [23], the temperature dependence of the thermal expansion can be fitted with a sum of T^2-linear term and the T^4-linear term of the lattice vibrations, as given by

$$\Delta\ell/\ell = AT^2 + BT^4, \tag{6.90}$$

where the length of the sample is denoted by ℓ. In the paramagnetic phase, the coefficient A increases toward the magnetic instability point. Its sign changes from positive to negative across the para- to ferromagnetic transition. They simply assumed that conduction electrons are responsible for the above T^2-linear dependence. However, the observed enhancement of A in the paramagnetic phase seems to suggest that it is caused by the magnetic origin (i.e., by the term $t^2\log[1/y_0(0)]$ to be explained later).

Forced Magneto-Striction at Low Temperatures In the case of weak external magnetic field where $\sigma \simeq \sigma_0(t)$ is satisfied, the temperature dependence of the constant $C_h(t)$ for the forced magneto-striction is generally given by (6.80). The analytic expression of its temperature dependence is available at low temperatures. According to (4.26), $U(t)$ decreases proportional to $T^2/[T_A\sigma_0^2(0)]^2$ with increasing temperature. The temperature dependence of the derivative $\partial U(t)/\partial\omega$ is also given by

$$\frac{\partial U(t)}{\partial \omega} = \frac{4+5r+r^2}{180cA^2(0,t_c)}(\gamma_m - \gamma_A)t^2 + \cdots . \tag{6.91}$$

Substituting (6.91), (4.24) for $V(t)/U(t)$, and (4.26) for $U(t)$ into (6.80), the t^2-linear dependence of $C_h(t)$ is given by

$$\frac{C_h(t)}{C_h(0)} = 1 + \frac{ct^2}{120A^2(0,t_c)}\left[(1-2g_A)\frac{4+5r+r^2}{3} - \frac{3+2r^2}{4}\right] + \cdots . \tag{6.92}$$

6.5.2 *Around the Critical Point*

The thermal component of the volume expansion in (6.55) at the critical temperature is given by

$$\frac{\omega_{th}(t_c)}{\omega_0} = 3\rho\kappa T_0\gamma_0 t_c^2 \int_0^{1/t_c} \mathrm{d}u\, u\Phi'(u) \simeq \frac{1}{4}\rho\kappa T_0\gamma_0 t_c^2 \log(1/t_c), \quad (t_c \ll 1) \tag{6.93}$$

where $u = x^3/t$. The temperature dependence of $\omega_{th}(t)$ is less affected by those of $y_0(t)$ and $y_{z0}(t)$ around $t = t_c$, as with the case of the specific heat.

On the other hand, the temperature dependence of the coupling constant $C_s(t)$ and the volume-striction $\omega_{zp}(t)$ are estimated by substituting the t dependence of $U(t)$ and $V(t)/U(t)$ in (4.38) for $t \lesssim t_c$ into (6.87).

$$\begin{aligned}
\frac{C_s(t)}{C_h(0)} &= \frac{14}{25c}(1-g_A)A(0,t_c)\left(\frac{40\sqrt{2}c}{7\pi t_c}\right)^2\left[1-\left(\frac{t}{t_c}\right)^{4/3}\right] + \cdots , \\
\frac{\omega_{zp}(t)}{\omega_0} &= \frac{98}{125c}(1-g_A)A(0,t_c)\left(\frac{40\sqrt{2}c}{7\pi t_c}\right)^2\left[1-\left(\frac{t}{t_c}\right)^{4/3}\right]^2 + \cdots .
\end{aligned} \tag{6.94}$$

They both vanish at the critical point in proportion to $(T-T_c)$ and $(T-T_c)^2$. The thermal expansion coefficient $\beta_{zp}(t)$ is therefore proportional to $(T-T_c)$. Contrary to this result, both the SEW and MU theories give a finite negative value of $\beta(t)$ in the limit $t \to t_c$, reflecting the temperature dependence of $M_0^2(T) \propto (T_c - T)$.

The temperature dependence is also estimated by (6.60) around t_c in the paramagnetic phase. The dependence of $U(t)$ and $V(t)/U(t)$ are then given by

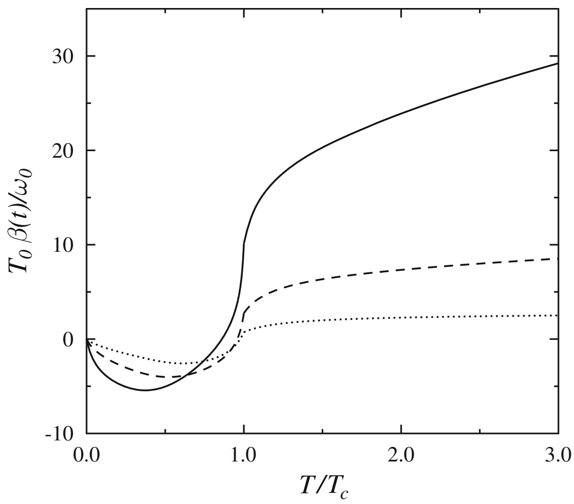

Fig. 6.2 Temperature dependence of the thermal expansion coefficient

$$U(t) = \frac{1}{2}[(t/t_c)^{4/3} - 1], \quad \frac{V(t)}{U(t)} = 2c\left(\frac{4}{\pi t_c}\right)^2 A(0, t_c)[(t/t_c)^{4/3} - 1]. \quad (6.95)$$

Substituting these results into (6.60) gives

$$\begin{aligned} \frac{\omega_{zp}(t)}{\omega_0} &= \frac{6c}{10}(1 - g_A)\left(\frac{4}{\pi t_c}\right)^2 A(0, t_c)[(t/t_c)^{4/3} - 1]^2, \\ \frac{C_s(t)}{C_h(0)} &= \frac{6c}{5}(1 - g_A)\left(\frac{4}{\pi t_c}\right)^2 A(0, t_c)[(t/t_c)^{4/3} - 1]. \end{aligned} \quad (6.96)$$

Both the MU and SEW theories predict the discontinuous change in the slope of the temperature dependence of the spontaneous magneto-striction $\omega_m(t)$, from the negative to the positive value (MU) and from the negative to zero (SEW), with increasing temperature. The above results of (6.94) and (6.96) predict the continuous change. The difference results from the temperature dependence of our magneto-volume coupling constant $C_s(t)$. Both the experiments of thermal expansion coefficient on $ZrZn_2$ by Ogawa, Kasai [24] and by Creuzet et al. [25] seem to support the continuous change. We show in Fig. 6.2, numerical results of the thermal expansion coefficient in the wide range of temperature from the order phase to the paramagnetic phase. The solid, dashed, and doted lines correspond to $t_c = 0.05, 0.1, 0.2$, respectively, for $g_0 = 0.1$ and $g_A = 0.1$.

Forced Magneto-Striction Around the Critical Point The temperature dependence of the forced magneto-volume coupling constant $C_h(t)$ is also evaluated by (6.80). The first term proportional to $V(t) \propto (t_c - t)^2$ is neglected since it is higher order than the second. The derivative $\partial U(t)/\partial\omega$ at the critical point is evaluated by using the temperature dependence of (4.38) for $U(t)$.

$$\left.\frac{\partial U(t)}{\partial \omega}\right|_{T=T_c} = \frac{28}{15}\left(\frac{T}{T_c}\right)^{4/3} \frac{\mathrm{d}\log T_c}{\mathrm{d}\omega} \simeq \frac{28}{15}\frac{\mathrm{d}\log T_c}{\mathrm{d}\omega}. \tag{6.97}$$

Putting the above result and (4.38) for $V(t)/U(t)$ into (6.80), the temperature dependence of $C_h(t)$ is given by

$$\begin{aligned}\frac{C_h(t)}{C_{h0}} &\simeq \frac{V(t)}{\gamma_m U(t)}\frac{\partial U(t)}{\partial \omega} \\ &= \frac{32c}{3}\left(\frac{4}{\pi t_c}\right)^2 A(0,t_c)\frac{1}{\gamma_m}\frac{\mathrm{d}\log T_c}{\mathrm{d}\omega}\left[1-\left(\frac{t}{t_c}\right)^{4/3}\right]+\cdots.\end{aligned} \tag{6.98}$$

It means that we can estimate the value of $\mathrm{d}\log T_c/\mathrm{d}\omega$ experimentally from the observed slope of the coupling constant $C_h(t)$ against $(T - T_c)$ around the critical temperature. We will show later, the value is represented in terms of γ_m, γ_0, and γ_A.

In the paramagnetic phase, the temperature dependence of $C_h(t)$ is evaluated by (6.78). Higher order term proportional to $V(t)$ is also neglected in this case. By putting (6.95) for $V(t)/U(t)$ into (6.78), the temperature dependence of $C_h(t)$ is given by

$$\frac{C_h(t)}{C_{h0}} = 2c(1-g_A+g_0)\left(\frac{4}{\pi t_c}\right)^2 A(0,t_c)\left[\left(\frac{t}{t_c}\right)^{4/3}-1\right]. \tag{6.99}$$

To summarize, the forced magneto-volume coupling constant $C_h(t)$ also decreased in proportion to $|T - T_c|$ toward the critical point in the same way as $C_s(t)$ for the spontaneous striction.

Critical Forced Magneto-Striction We have already shown in Chap. 3 that the magnetic isotherm at the critical point exhibits the anomalous behavior under the influence of critical spin fluctuations. The same behavior is also expected for the forced magneto-striction, because it is given by the volume derivative of the same free energy. The critical forced magneto-striction can be treated according to the general formula in (6.70). Both the σ dependence of $y(\sigma, t)$ and the ω-derivative $\partial y(\sigma, t)/\partial\omega$ are then necessary. These are determined by solving the simultaneous differential equations (6.71) and (6.72).

Substituting the critical behaviors, $A'(y, t) \propto 1/\sqrt{y}$ and $A'(y_z, t) \propto 1/\sqrt{y_z}$, for the thermal fluctuation amplitudes, (6.72) is written by

$$-\frac{\pi t_c}{8}\left(\frac{2}{\sqrt{y}}\frac{\partial y}{\partial \omega}+\frac{1}{\sqrt{y_z}}\frac{\partial y_z}{\partial \omega}\right) = 3A(0,t_c)\gamma_m(1-g_A-g_0), \tag{6.100}$$

where the higher order terms with respect to σ^2 are neglected. At the critical point, both $y(\sigma, t_c)$ and $y_z(\sigma, t_c)$ are proportional to σ^4, as was already shown in Chap. 3. Then the derivative $\partial y(\sigma, t_c)/\partial\omega$ has to be proportional to σ^2, and therefore $\partial y_z(\sigma, t_c)/\partial\omega = 3\partial y(\sigma, t_c)/\partial\omega$ is derived from the relation between $y(\sigma, t)$ and

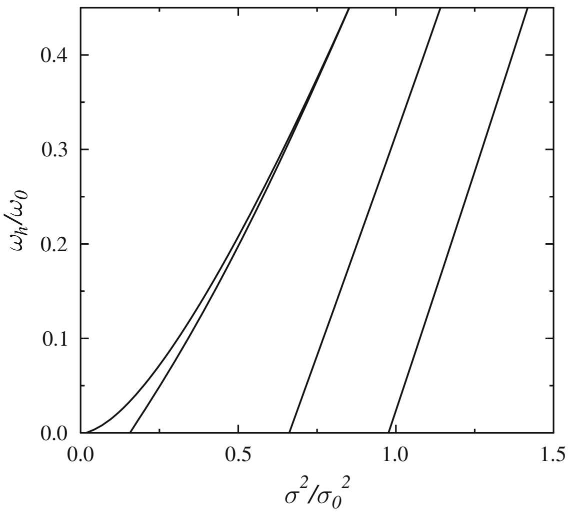

Fig. 6.3 Numerically estimated forced magneto-striction at temperatures $T/T_c = 0.10, 0.50, 0.90, 0.99$ from the right for $T_c/T_0 = 0.05$

$y_z(\sigma, t)$. The σ^2-linear coefficient of $\partial y(\sigma, t_c)/\partial\omega$ is determined as follows:

$$\frac{1}{\gamma_m}\frac{\partial y(\sigma, t_c)}{\partial\omega} = -\frac{24\sqrt{5}}{3+2\sqrt{5}}(1 - g_A - g_0)\frac{\sqrt{y_c}}{\pi t_c}A(0, t_c)\sigma^2.$$

Substituting the result into (6.70) finally leads to the critical forced magneto-striction given by

$$\frac{\omega_h(\sigma, t_c)}{\omega_0} = \frac{12\sqrt{5}}{3+2\sqrt{5}}(1 - g_A - g_0)\frac{\sqrt{y_c}}{\pi t_c y_1(0)}A(0, t_c)\frac{\sigma^4}{\sigma_0^4(0)}. \tag{6.101}$$

We show in Fig. 6.3, the numerically estimated σ dependence of the forced magneto-striction in the ordered phase by solving the simultaneous differential equations (6.71), (6.72), and (6.74). Relative volume-strictions $\omega_h(\sigma, t)/\omega_0$ at temperatures, $T/T_c = 0.10,\ 0.50,\ 0.90,\ 0.99$, are plotted against $\sigma^2/\sigma_0^2(0)$. At low temperatures, good linearity is observed because of the weak σ dependence of the coupling constant $C_h(\sigma, t)$. Since the coupling constant $C_h(t)$ decreases to zero toward the critical point in accordance with (6.98), the σ^4-linear behavior is expected to emerge around the critical temperature. The behavior is actually observed in Fig. 6.3 as the result at $T/T_c = 0.99$. It is evident from this figure that the σ^2-linear behavior at low temperatures changes to the critical σ^4-linear behavior with increasing temperature.

Forced Magneto-Striction Observed in MnSi In the field of itinerant electron magnetism, not enough attention have long been payed on the concept of the critical magnetic isotherm. The same is true for the critical forced magneto-striction. Although the anomalous forced magneto-striction seemed to be observed in MnSi at the critical temperature, it did not attract much attention until Takahashi [26] pointed

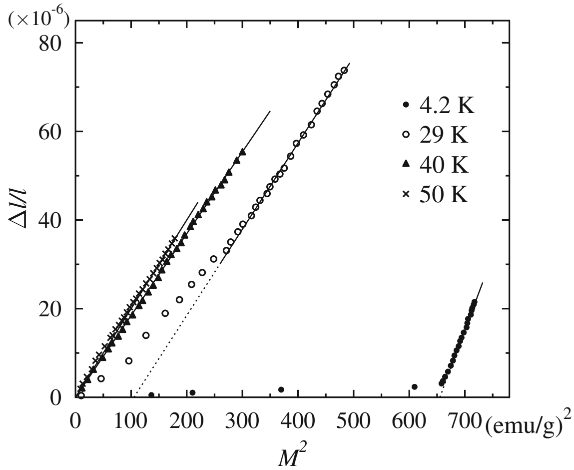

Fig. 6.4 Observed forced magneto-striction in MnSi (Matsunaga et al. [6])

out its relevance to the critical forced magneto-striction. We show in Fig. 6.4 the forced magneto-striction of MnSi observed by Matsunaga et al. cited from Fig. 8 of [6]. In this figure, observed forced-strictions (relative changes of the length of the sample, $\Delta\ell/\ell$) are plotted against M^2. The plot considerably deviates from the linearity around the critical temperature $T_c \simeq 30$ K. The good linearity is, however, confirmed by plotting the data against M^4 at $T = 29$ K. There seem to be no other observed critical forced magneto-striction at present.

6.5.3 *In the Paramagnetic Phase*

Spontaneous Magneto-Striction The magneto-volume effect observed at higher temperatures in the paramagnetic phase, where the Curie-Weiss law temperature dependence of the magnetic susceptibility is observed, is discussed in this section. In the region where the Curie-Weiss law of the inverse of the magnetic susceptibility in (3.44), i.e., $y_0(t) \simeq 2(t-t_c)/[5cy_1(0)p_{\rm eff}^2]$, is satisfied, the temperature dependence of $y_1(t)$ is negligible. Then $V(t)/U(t) = y_1(t)/y_1(0)$ is almost independent of temperature and $V(t)$ is given by

$$V(t) = \frac{y_0(t)}{y_1(0)\sigma_0^2(0)} \simeq \frac{c}{10A^2(0,t_c)}\frac{p_s^2}{p_{\rm eff}^2}(t-t_c), \tag{6.102}$$

by using $A(0,t_c) = cy_1(0)\sigma_0^2(0)$. According to (6.60), the ratio $C_s(t)/C_h(0)$, as given below, is about $3(1-g_A)/5$.

$$\frac{C_s(t)}{C_h(0)} = \frac{3}{5}(1-g_A)\frac{y_1(t)}{y_1(0)} \simeq \frac{3}{5}(1-g_A). \quad (6.103)$$

The temperature dependence of the thermal expansion $\omega_{zp}(t)$ in the same (6.60) is given by

$$\frac{\omega_{zp}(t)}{\omega_0} = \frac{C_s(t)}{C_h(0)}\frac{y_0(t)}{y_1(t)\sigma_0^2(0)} = \frac{3}{5}(1-g_A)V(t)$$
$$\simeq \frac{3(1-g_A)c}{50A^2(0,t_c)}\frac{p_s^2}{p_{\text{eff}}^2}(t-t_c). \quad (6.104)$$

The thermal expansion coefficient then becomes almost temperature independent as given by

$$\frac{T_c\beta_{zp}(t)}{\omega_0} = \frac{T_c}{\omega_0 T_0}\frac{\mathrm{d}\omega_{zp}(t)}{\mathrm{d}t} \simeq \frac{3}{50}\frac{c(1-g_A)t_c}{A^2(0,t_c)}\frac{p_s^2}{p_{\text{eff}}^2} = \frac{27c(1-g_A)}{50(C_{4/3})^2 t_c^{5/3}}\frac{p_s^2}{p_{\text{eff}}^2}. \quad (6.105)$$

Note that the close relation is satisfied between the ratio of moments p_{eff}/p_s and $t_c = T_c/T_0$ as shown in Sect. 3.3.4. The right hand side of (6.105) is determined by the single parameter t_c.

The validity of (6.105) can be confirmed experimentally. The value of $\beta_{zp}(t)$ in the paramagnetic phase is determined by extracting the temperature independent component from the observed thermal expansion coefficient. The value of ω_0 is estimated from the observed forced magneto-volume constant $C_h(0)$ at low temperatures and the spontaneous magnetization squared $\sigma_0^2(0)$. It is, however, not so easy to extract the magnetic contribution from the total volume expansion by subtracting those from the lattice vibrations and etc. The value of $T_c\beta/\omega_0$ estimated in this way by using available data from references are plotted against the ratio T_c/T_0 in Fig. 6.5. In the same figure, numerically estimated values of the right hand side of (6.105) is plotted by the solid curve. Though the factor $(1-g_A)$ is not included in the plot, raw experimental data from references are employed.

The figure shows that solid circles of experiments fall fairly close to the theoretical curve. According to (6.103) and (6.104), the ratio $T_c\beta/\omega_0$ is closely related to the coupling ratio $C_s(t)/C_h(0)$. The observed data in the figure also support the theoretical prediction for the ratio smaller than 1.

Forced Magneto-Striction We have already shown in Sect. 6.4 that the forced magneto-striction in the paramagnetic phase is given by $\omega_h(t) = \rho\kappa C_h(t)\sigma^2$, and the temperature dependence of the coupling constant $C_h(t)$ is described by (6.78). The value of $C_h(t)$ has the general tendency to saturate with increasing temperature in the paramagnetic phase. In cases with non-negligible size of g_A, however, it will show a slight increase, because of the presence of $(t-t_c)$-linear term of $U(t)$ in this (6.78).

According to (6.75), the volume derivative $\partial y_0(t)/\partial\omega$ is necessary to evaluate the coupling constant $C_h(t)$. The value of this derivative is also closely related to

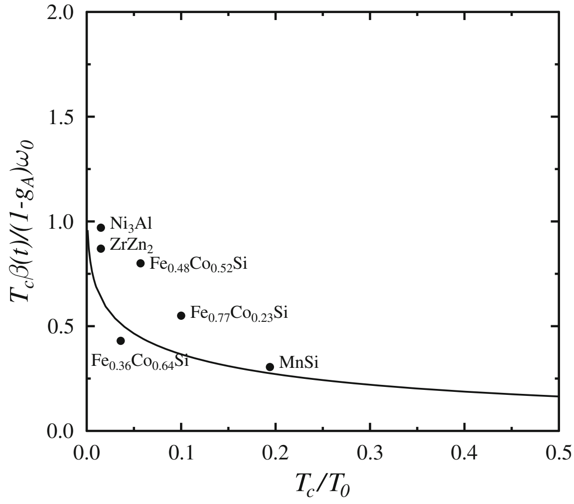

Fig. 6.5 Observed thermal expansion coefficients in the paramagnetic phase versus T_c/T_0 by Takahashi and Nakano [20]

the pressure effect measurements of the paramagnetic susceptibility by Brommer et al. [27]. They reported that the temperature dependence of the derivative $\mathrm{d}\log\chi(T)/\mathrm{d}\omega$ for Ni_3Al and TiCo is proportional to the magnetic susceptibility $\chi(T)$, i.e., $\mathrm{d}\log\chi(T)/\mathrm{d}\omega \propto \chi(T)$. In other words, the value of $\chi^{-2}(T)\mathrm{d}\chi(T)/\mathrm{d}\omega$, and therefore $\mathrm{d}\chi^{-1}(T)/\mathrm{d}\omega$ is independent of temperature, being in agreement with (6.77). Values of $\mathrm{d}\log\chi(T)/\mathrm{d}\log V$ for Ni_3Al observed by them at three temperatures are shown in Fig. 6.6 against $\chi(T)$. They fall on a straight line with a positive slope as shown in this figure. The slope of the figure is also represented in our

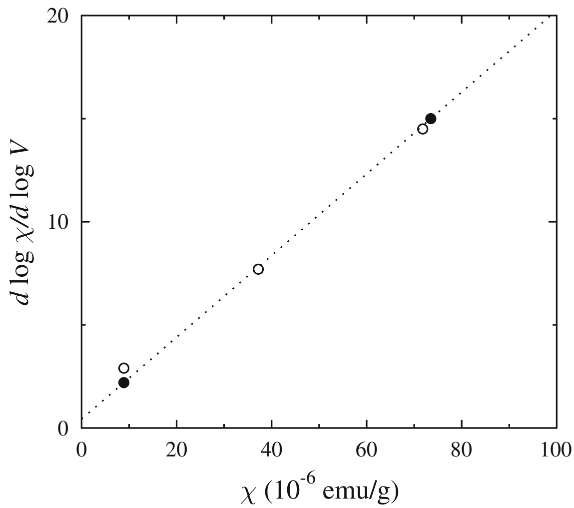

Fig. 6.6 Pressure effect on paramagnetic susceptibility of Ni_3Al by Brommer et al. (*solids circles* are results by levitation method)

theoretical notations as

$$\frac{N_0}{2\chi}\frac{\mathrm{d}\log\chi}{\mathrm{d}\ln V} = -T_A y_0(t)\frac{\partial \log y_0(t)}{\partial\omega} = -T_A\frac{\partial y_0(t)}{\partial\omega}$$
$$= T_A y_1(t)\sigma_0^2(0)\frac{\mathrm{d}\log A(0,t_c)}{\mathrm{d}\omega} \tag{6.106}$$

The value of the above left hand side is estimated to be 2.73×10^3 K for $Ni_{74.8}Al_{25.2}$ from the observed data by Brommer et al. Spectral parameters of spin fluctuations in this compound are already estimated to be $T_0 \simeq 3 \times 10^3$ K and $T_A \simeq 3 \times 10^4$ K, giving $y_1(t) \simeq y_1(0) \simeq 1/3$. The volume-striction in the right-hand side is also estimated to be

$$\frac{\mathrm{d}\log A(0,t_c)}{\mathrm{d}\omega} = -B\frac{\mathrm{d}\log A(0,t_c)}{\mathrm{d}p} = -B\frac{\mathrm{d}\log\sigma_0^2(0)}{\mathrm{d}p} \simeq 46.2, \tag{6.107}$$

where $B = 1.7$ M bar as a bulk modulus and $\mathrm{d}\log\sigma_0^2(0)/\mathrm{d}p = 27.2$. Effects of γ_0 and γ_A are neglected as a rough estimate. If we finally assume $\sigma_0(0) = 0.05$ or 0.07 as the spontaneous magnetization, the right hand side of (6.106) is given by 1.15×10^3 K or 2.26×10^3 K, respectively, in nearly close agreement with the estimate by Brommer et al.

6.5.4 Numerical Results on Volume-Strictions

Numerical results of the temperature dependence of spontaneous magneto-volume striction by Takahashi and Nakano [20] are shown in Fig. 6.7. Dashed, dotted, and solid lines correspond to the components $\omega_{th}(t)$, $\omega_{zp}(t)$ of the thermal expansion, and the sum of the both, respectively, for $t_c = 0.01, 0.05, 0.1$, in descending order from the top. It is interesting to notice that the relative ratio of the thermal fluctuation component to the total thermal expansion becomes larger for smaller value of t_c. It will cancel the increase of $\omega_{zp}(t)$ below the critical temperature with decreasing temperature. Thermal expansion will then become monotonically increasing function. Note that the relative volume-striction divided by ω_0 is plotted in this figure. The smaller the value of t_c, the value of ω_0 becomes smaller. The magnitude of this figure is nothing to do with the absolute value of the thermal expansion.

The enhancement of the thermal expansion coefficients at low temperatures is shown in Fig. 6.8. The t-linear coefficient of the thermal expansion coefficient, $[\beta_t(t) + \Delta\beta(t)]/3\rho\kappa\gamma_0 T$, is plotted against T/T_c in this figure. Solid, dashed, dot-dashed, and dotted curves from the top corresponds to $t_c = 0.005, 0.01, 0.05, 0.1$, respectively. The value of $\sigma_0(0)$ increases in this order, whereas the enhancement decreases inversely. We finally show in Fig. 6.9, the temperature dependence of the spontaneous (thin lines) and the forced (thick lines) magneto-coupling constants,

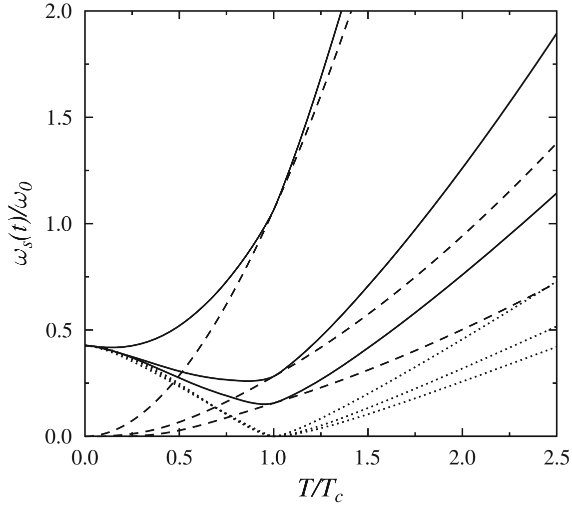

Fig. 6.7 Numerically estimated temperature dependence of spontaneous magneto-striction, for $g_0 = g_A = 0.1$ and $T_A/T_0 = 10$

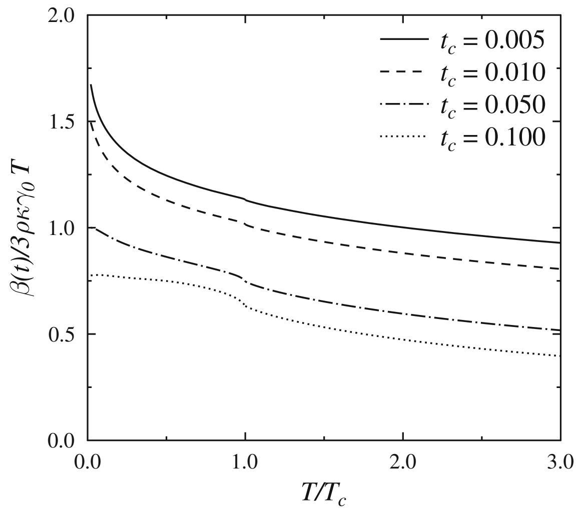

Fig. 6.8 Enhancement of the t-linear coefficient of the thermal expansion coefficient at low temperatures [20]

$C_s(t)$ and $C_h(t)$. Solid, dashed, and dotted curves correspond to $t_c = 0.01, 0.05, 0.1$, respectively.

6.6 Magneto-Volume Effect for Paramagnets

From the similarity between magnetic isotherms for ferromagnets and paramagnets near the magnetic instability point, we show in Chap. 3, that the value of $\sigma_p^2(0) \equiv y_0(0)/y_1(0)$ defined in (3.21) for paramagnets corresponds to the spontaneous

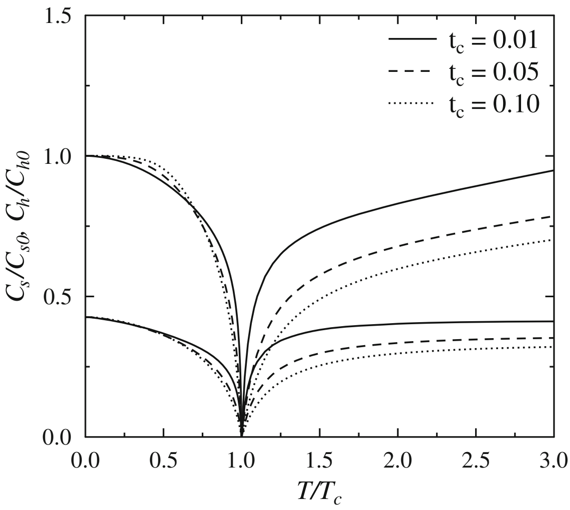

Fig. 6.9 Temperature dependence of magneto-volume coupling constants, $C_s(t)$ and $C_h(t)$, for $T_A/T_0 = 10$ [20]

magnetic moment squared $\sigma_0^2(0)$ for ferromagnets. From the same analogy, the Grüneisen parameter γ_m for paramagnets is also defined by

$$\Delta\left\langle S_{\text{loc}}^2\right\rangle = -\frac{3}{5}\sigma_p^2(0), \quad \frac{\mathrm{d}\Delta\left\langle S_{\text{loc}}^2\right\rangle}{\mathrm{d}\omega} = \frac{3}{5}\gamma_m\sigma_p^2(0). \tag{6.108}$$

The negative value of $\Delta\left\langle S_{\text{loc}}^2\right\rangle$ is characteristic to paramagnets. Corresponding to the definitions of the coupling constant $C_h(0)$ and ω_0 for ferromagnets, (6.50) and (6.61), the same parameters can be defined by

$$C_{h0} = T_A y_0(0)\gamma_m, \quad \omega_0 = \rho\kappa C_{h0}\sigma_p^2(0). \tag{6.109}$$

Note, however, the above forced magneto-volume coupling C_{h0} is slightly different from the value $C_h(0)$ in the ground state ($t = 0$), as will be shown later. We also define the reduced parameters $V(t)$ and $U(t)$ by

$$V(t) = \frac{y_0(t)}{y_0(0)}, \quad U(t) = \frac{y_0(t)}{y_0(0)}\frac{y_1(0)}{y_1(t)} = \frac{\sigma_p^2(t)}{\sigma_p^2(0)} \tag{6.110}$$

as scaled values of $y_0(t)$ and $\sigma_p^2(t)$. In the next subsection, we first deal with the temperature dependence of the spontaneous magneto-striction, followed by the forced magneto-volume striction.

6.6.1 Spontaneous Magneto-Striction for Paramagnets

Along with the case of ferromagnets, the thermal component of the volume-strain in this case is also obtained by (6.55), except for $u_z = u$ because of the absence of the spontaneous magnetization. The component $\omega_{zp}(t)$ is also evaluated, according to the general definition (6.35) and (6.36). The coefficient C_{zp} is evaluated by the volume derivative of the free energy F_{zp}, the volume dependence of which is characterized by the Grüneisen parameters defined in (6.108) and (6.37). They are given by

$$\begin{aligned}\frac{\omega_{th}(t)}{\omega_0} &= \frac{3g_0 t}{5cy_0^2(0)}\int_0^1 \mathrm{d}x x^2 u\Phi'(u),\\ \omega_{zp}(t) &= 3\rho\kappa C_{zp} y_0(t) = \frac{3}{5}\rho\kappa C_{h0}\sigma_p^2(0)(1+g_A)\frac{y_0(t)}{y_0(0)}\\ &= \frac{3}{5}\omega_0(1+g_A)V(t),\\ C_{zp} &= \frac{1}{3}\frac{\partial}{\partial\omega}\left[T_A \Delta\left\langle S_{\mathrm{loc}}^2\right\rangle\right] = \frac{1}{5}T_A\sigma_p^2(0)(\gamma_m+\gamma_A).\end{aligned} \tag{6.111}$$

These results in (6.111) correspond to (6.55) for ferromagnets. We cannot define the magneto-volume coupling constant literally for paramagnets with no spontaneous magnetic moment. We have, however, intentionally defined the coefficient $C_s(t)$ from the similarity with ferromagnets.

$$\omega_{zp}(t) = \rho\kappa C_s(t)\sigma_p^2(t), \quad \frac{C_s(t)}{C_{h0}} = \frac{3V(t)}{5U(t)}(1+g_A). \tag{6.112}$$

The thermal expansion coefficient is also given by the temperature derivative of (6.111).

$$\begin{aligned}\frac{1}{\omega_0}\frac{\mathrm{d}\omega_m(t)}{\mathrm{d}t} &= \bar\beta(t) = \bar\beta_{th}(t) + \bar\beta_{zp}(t),\\ \bar\beta_{th}(t) &= \frac{g_0}{5c_z y_0^2(0)}\left\{-3\int_0^1 \mathrm{d}x x^2 u^2 \Phi''(u)\right.\\ &\qquad\left. + 2y_0(0)\frac{\mathrm{d}V(t)}{\mathrm{d}t}\left[A(y_0,t) - t\frac{\partial A(y_0,t)}{\partial t}\right]\right\},\\ \bar\beta_{zp}(t) &= \frac{3}{5}(1+g_A)V'(t).\end{aligned} \tag{6.113}$$

In analogy with (6.83) for ferromagnets in the ordered phase, the thermal component of the volume expansion $\omega_{th}(t)$ at low temperatures is approximated by

$$\omega_{th}(t) = \frac{3}{8}\rho\kappa\gamma_0 t^2 \log y_0^{-1}(0) + \cdots . \tag{6.114}$$

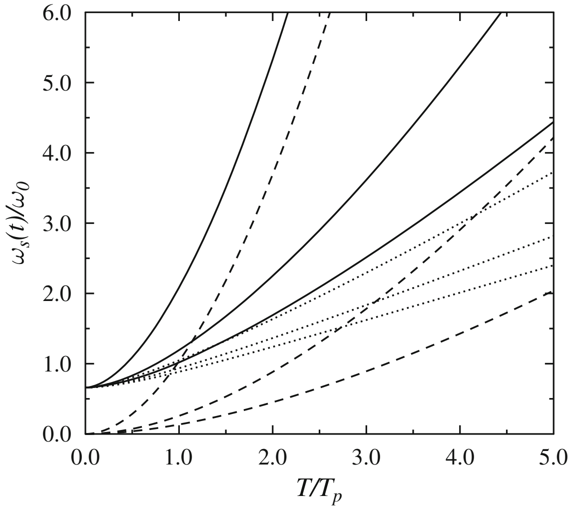

Fig. 6.10 Temperature dependence of magneto-volume strictions of paramagnets

On the other hand, $\omega_{zp}(t)$ is given by

$$\frac{\omega_{zp}(t)}{\omega_0} = \frac{3}{5}(1+g_A)\left[1 + \frac{t^2}{24cy_0^2(0)} + \cdots\right]. \tag{6.115}$$

by putting the temperature dependence of $y_0(t)$ into (6.111). The total magneto-volume striction is therefore given by

$$\frac{\omega_m(t)}{\omega_0} = \frac{3}{5}(1+g_A) + \frac{t^2}{40cy_0^2(0)}[g_0 \log y_0^{-1}(0) + 1 + g_A] + \cdots. \tag{6.116}$$

Nearly the same behavior is thus expected at higher temperatures, independent of ferro- and paramagnets, where the Curie-Weiss law of the magnetic susceptibility is observed.

In Fig. 6.10, numerically estimated temperature dependence of the magneto-volume strictions of (6.111) is shown. The results for components, $\omega_{th}(t)$ and $\omega_{zp}(t)$, and the sum of them are shown by dashed, dotted, and solid curves, respectively, for $t_p = 0.01, 0.05, 0.10$ from the top in descending order. The numerical results for the t-linear coefficient of the thermal expansion coefficient, i.e., $\beta(t)/3\rho\kappa\gamma_m T$, are also shown in Fig. 6.11. The enhancement of this t-linear coefficient at low temperatures in this figure results from the factor $\log y_0^{-1}(0)$ in (6.114).

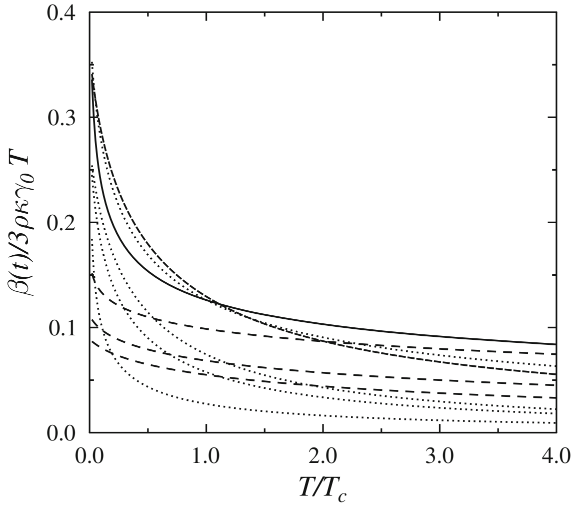

Fig. 6.11 Temperature dependence of $\beta(t)/3\rho\kappa\gamma_m T$ with the same parameters t_P as Fig. 6.10

6.6.2 Forced Magneto-Striction for Paramagnets

Forced magneto-volume striction $\omega_h(\sigma, t)$ is generally given by the σ derivative of (6.46). In the weak external magnetic field limit, $\omega_h(\sigma, t) = \rho\kappa C_h(t)\sigma^2$ is satisfied with coupling constant $C_h(t)$ in (6.75). The ω-derivative $\partial y_0(t)/\omega$ in this equation is evaluated by differentiating (3.30) with respect to ω, i.e.,

$$A(y_0, t) - c_z y_0(t) = -c y_0(0) = -A(0, t_p), \tag{6.117}$$

for paramagnets. It is given by

$$\begin{aligned}[A'(y_0, t) - c]\frac{\partial y_0(t)}{\partial\omega} &= -\frac{c y_1(0)}{y_1(t)}\frac{\partial y_0(t)}{\partial\omega} \\ &= -c\frac{\partial y_0(0)}{\partial\omega} = c(\gamma_m + \gamma_A - \gamma_0) y_0(0),\end{aligned} \tag{6.118}$$

with the use of (3.50) for $y_1(t)$. The right hand side is derived from the ω derivative of the relation $y_0(0) = T_A\sigma_p^2(0)/15T_0$ in (3.21).

$$\frac{1}{y_0(0)}\frac{\mathrm{d}y_0(0)}{\mathrm{d}\omega} = \frac{\mathrm{d}\log y_0(0)}{\mathrm{d}\omega} = -\gamma_m - \gamma_A + \gamma_0. \tag{6.119}$$

The derivative $\partial y_0(t)/\omega$ is therefore finally given by

$$\frac{\partial y_0(t)}{\partial\omega} = -\frac{y_1(t)}{y_1(0)}(\gamma_m + \gamma_A - \gamma_0) y_0(0). \tag{6.120}$$

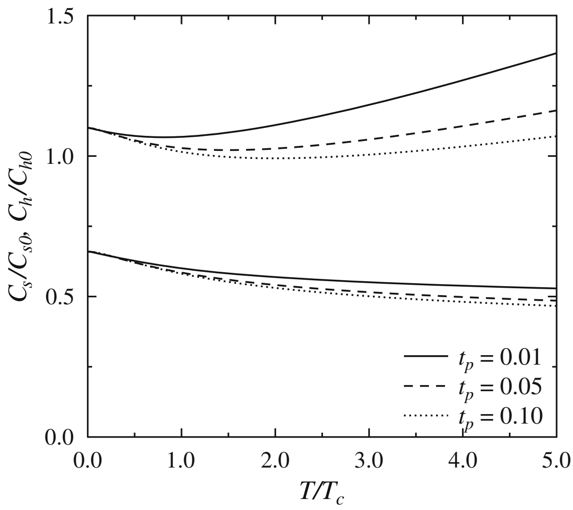

Fig. 6.12 Numerically estimated temperature dependence of the magneto-volume coupling constants $C_s(t)$ and $C_h(t)$ for paramagnets for $t_p = 0.01,\ 0.05$, and 0.10

It corresponds to (6.77) for ferromagnets. Substitution of (6.120) into (6.75) gives

$$\frac{C_h(t)}{C_{h0}} = V(t)\left[g_A + (1 + g_A - g_0)\frac{1}{U(t)}\right] = \frac{V(t)}{U(t)}\{1 + g_A[1 + U(t)] - g_0\} \tag{6.121}$$

Numerically estimated results of (6.112) for $C_s(t)$ and (6.121) for $C_h(t)$ are shown in Fig. 6.12.

6.7 Pressure Effects on Spontaneous Magnetic Moment and the Critical Temperature

We mentioned, at the beginning of this chapter, that the volume change of magnets induces changes of their spontaneous magnetic moment $\sigma_0(0)$ in the ground state and the Curie temperature T_c. According to the definition of the Grüneisen parameter in (6.39), the volume change of $\sigma_0(0)$ is characterized by the parameter γ_m. In this last section, we first show how the volume dependence of the critical temperature T_c is described in terms of Grüneisen parameters.

6.7.1 Effect of Pressure on the Critical Temperature

The critical temperature is determined by the condition, $y_0(t_c) = 0$, for the inverse of the magnetic susceptibility. Along with the SEW theory in Sect. 6.3.1, the change of the critical temperature δT_c against the volume change can be determined by this condition. Let us first note the following relation between $\delta\omega$ and δT_c derived by the condition:

$$\left.\frac{\partial y_0(t)}{\partial t}\right|_{t=t_c}\left(\frac{\delta T_c}{T_0}-\frac{T_c}{T_0^2}\delta T_0\right)+\left.\frac{\partial y_0(t)}{\partial \omega}\right|_{t=t_c}\delta\omega=0. \tag{6.122}$$

With the use of (3.30) for $y_0(t)$, the above two partial derivatives of $y_0(t)$ can be represented as (5.32) and (6.77), i.e.,

$$\frac{\partial y_0(t)}{\partial t}=\frac{y_1(t)}{cy_1(0)}\frac{\partial A(y_0,t)}{\partial t},\quad \frac{\partial y_0(t)}{\partial \omega}=-\frac{y_1(t)}{cy_1(0)}\frac{\partial A(0,t_c)}{\partial \omega}. \tag{6.123}$$

They are given by the partial derivatives of (3.30) with respect to t and ω, respectively. Equation (6.122) is then written in the form

$$\frac{\partial A(0,t_c)}{\partial t_c}\frac{T_c}{T_0}\left(\frac{\delta T_c}{T_c}-\frac{\delta T_0}{T_0}\right)-\frac{\partial A(0,t_c)}{\partial \omega}\delta\omega=0,$$

where the limit $t\to t_c$ is taken after dividing the both sides by $y_1(t)/cy_1(0)$. Substituting (6.73) for the derivative $\partial A(0,t_c)/\partial\omega$, (6.122) is given by

$$t_c\frac{\partial A(0,t_c)}{\partial t_c}\left(\frac{\mathrm{d}\log T_c}{\mathrm{d}\omega}+\gamma_0\right)=(\gamma_m-\gamma_A+\gamma_0)A(0,t_c).$$

In the above left-hand side, the following relation is satisfied, because of $A(0,t_c)\propto t_c^{4/3}$ in (3.21) for $t_c\ll 1$.

$$t_c\frac{\partial A(0,t_c)}{\partial t_c}=\frac{4}{3}A(0,t_c).$$

As a result, the following relation is satisfied for the volume effect on the critical temperature T_c.

$$\frac{4}{3}\frac{\mathrm{d}\log T_c}{\mathrm{d}\omega}=\gamma_m-\gamma_A-\frac{1}{3}\gamma_0,\quad \frac{\mathrm{d}\log\sigma_0^2(0)}{\mathrm{d}\omega}=\gamma_m. \tag{6.124}$$

The definition of the parameter γ_m is also shown for reference.

The above result (6.124) is equivalent to the relation (3.11) in Chap. 3, i.e.,

$$\sigma_0^2(0)=\frac{5C_{4/3}T_0}{T_A}\left(\frac{T_c}{T_0}\right)^{4/3}, \tag{6.125}$$

which is satisfied between $t_c=T_c/T_0$ and $\sigma_0^2(0)$, irrespective of the volume change. The same relation as (6.124) is derived from the volume derivative of the both sides of (6.125). Note that multiple Grüneisen parameters are involved in (6.124). The result is reasonable, because phase transitions at finite temperatures are affected by spin fluctuations, the time dependence and the spatial variation of which are characterized by parameters γ_0 and γ_A.

As the effect of external pressure, (6.124) can be written in the form

$$\begin{aligned} \frac{4}{3}\frac{\mathrm{d}\log T_c}{\mathrm{d}p} &= -\frac{4}{3}\kappa\frac{\mathrm{d}\log T_c}{\mathrm{d}\omega} = -\kappa(\gamma_m - \gamma_A - \gamma_0/3), \\ \frac{\mathrm{d}\log \sigma_0^2(0)}{\mathrm{d}p} &= -\kappa\gamma_m. \end{aligned} \tag{6.126}$$

by introducing the compressibility κ. It is also rewritten as

$$\frac{\mathrm{d}\log T_c}{\mathrm{d}p} - \frac{3}{4}\frac{\mathrm{d}\log \sigma_0^2(0)}{\mathrm{d}p} = \frac{\kappa}{4}(3\gamma_A + \gamma_0) \equiv \kappa\gamma_{0,A}, \tag{6.127}$$

by eliminating the parameter γ_m from them. We have already shown in (3.13), the fourth expansion coefficient F_1 of the free energy in powers of the magnetization M is expressed in terms of spectral parameters T_0 and T_A. The pressure effect on F_1 is then given by

$$\frac{\mathrm{d}\log F_1}{\mathrm{d}p} = 2\kappa\gamma_A - \kappa\gamma_0. \tag{6.128}$$

We can estimate the value of F_1 experimentally from the slope of the Arrott plot of the observed magnetization curve. From the slope of its pressure dependence against the pressure, the pressure derivative of F_1 is estimated. As solutions of a simultaneous equation of (6.127) and (6.128), parameters γ_0 and γ_A are now represented as follows:

$$\begin{aligned} \kappa\gamma_A &= \frac{4}{5}\frac{\mathrm{d}\log T_c}{\mathrm{d}p} - \frac{3}{5}\frac{\mathrm{d}\log \sigma_0^2(0)}{\mathrm{d}p} + \frac{1}{5}\frac{\mathrm{d}\log F_1}{\mathrm{d}p}, \\ \kappa\gamma_0 &= \frac{8}{5}\frac{\mathrm{d}\log T_c}{\mathrm{d}p} - \frac{6}{5}\frac{\mathrm{d}\log \sigma_0^2(0)}{\mathrm{d}p} - \frac{3}{5}\frac{\mathrm{d}\log F_1}{\mathrm{d}p}. \end{aligned} \tag{6.129}$$

In order to evaluate the magnetic Grüneisen parameters experimentally, the value of γ_m in (6.126) is estimated from the slope of the variation of $\sigma_0^2(0)$ against the pressure p. For the rest of parameters, γ_A and γ_0 in (6.129), additional pressure effect measurements of T_c and F_1 are needed.

One of the distinct features of the theory of magneto-volume effects in this book, compared to the SEW and MU theories, is that spectral parameters T_0 and T_A are volume dependent. It is reflected in the relation (6.127) between the pressure effects on $\sigma_0(0)$ and T_c. The SEW theory predicts the relation, $\mathrm{d}\log\sigma_0(0)/\mathrm{d}p = \mathrm{d}\log T_c/\mathrm{d}p$, since $\sigma_0^2(0) \propto T_c^2$ is satisfied. In the MU theory, on the other hand, the same relation (6.127) is satisfied, but with $\gamma_{0,A} = 0$ in the right hand side. Validity of them are verified by the pressure effect measurements of $\sigma_0(0)$ and T_c.

Many experiments have been done on the pressure effects on $\sigma_0(0)$ and T_c. According to Kanomata (T. Kanomata, Private Commun.), the observed results show variety of signs dependent on each itinerant electron magnets against the applied pressure. Most of them are, however, classified into the following three categories:

1. Both the change of $\sigma_0(0)$ and T_c have the same signs.
   This case is characteristic to itinerant electron magnets.
2. Though T_c changes, the value of $\sigma_0(0)$ remains almost unchanged.
   It is usually observed for localized electron magnets.
3. Each of them show changes with different signs.

These properties can be understood by introducing multiple Grüneisen parameters, and in some cases by assuming that they are of comparable magnitude. They will be interpreted associated with signs and relative magnitudes of these parameters.

6.7.2 Pressure Effect Measurements of Spontaneous Magnetic Moment and Critical Temperature

A large number of experiments on the magneto-volume effects had been reported from the late 1960s to the beginning of 1980s. Their aim was to verify the SEW theory experimentally. Analyses of experiments were also based on the theory. These were reviewed by Franse [28, 29]. Later, magneto-volume effects on $ZrZn_2$, MnSi, and Ni_3Al were reported by Brommer and Franse [30]. Results of analyses based on the MU theory were also found here. These authors also published the handbook on the magneto-volume effects in 1990 [31]. Most of these experiments belong to the first category of the Kanomata's classification. The observed large T^2-linear thermal expansions for para- and ferromagnets near the magnetic instability points should be rather associated with magnetic origins. They were, however, regarded as the effect of conduction electrons from the conventional view. Many magneto-volume properties reported up to the present need to be re-examined.

The following is a brief summary of observed magneto-volume effects on weak itinerant electron ferromagnets where weak spontaneous magnetization are observed.

Ni_3Al

So far, a number of magneto-volume measurements have been done on this compound. The M^2-linear coefficients of the free energy were estimated by Buis et al. [32] from the observed magnetic isotherms under the pressure up to 5 kbar. The pressure dependence of the critical temperature T_c and the value of the magneto-volume coupling constant C are then evaluated by their temperature and magnetic field dependence. The critical temperature was determined as the temperature at which the Arrott plot of the magnetization curve passes through the origin. These values vary within the range, $\partial T_c/\partial p = -0.58 \sim -0.36$ K/kbar and $C \times 10^{-6} = 0.12 \sim 0.16$ (g/cm^3), depending on the composition of Ni and Al, according to their report. As a compressibility, $\kappa = 4.2 \times 10^{-13}$ cm^2/dyne was employed. The forced magneto-volume coupling constant C was also estimated by Kortekaas and Franse [4] from the magneto-striction measurements in the ordered phase. From the observed constants at different temperatures, they showed that C is temperature dependent, that presumably originates from the T^2/T_F^2 dependence of the SEW theory. The value of the coupling $\rho\kappa C \times 10^6 \sim 0.6$ ($G^{-2}g^2cm^{-6}$) at 4.2 K is reduced by 0.4 at T_c. As the compressibility, $\kappa = 4.18 \times 10^{-13}$ cm^2/dyne was used to estimate the value of C.

On the other hand, Buis et al. [33] made magnetization measurements on samples under pressure with different Al composition of the compounds. From the analysis of the composition dependence of the M^2 expansion coefficient (i.e., the inverse of the magnetic susceptibility) of the free energy, they predicted the value of the spontaneous magnetic moment and the pressure dependence of the critical temperature of the ideal Ni_3Al compound [33] with $\sigma_0 = 0.077\ \mu_B$/at and $T_c = 63$ K as given by

$$\frac{\partial \log \sigma_0(0)}{\partial p} = -5.29\ \text{Mbar}^{-1}, \quad \frac{\partial \log T_c}{\partial p} = -6.35\ \text{Mbar}^{-1}.$$

The pressure dependence of the magnetic susceptibility in the paramagnetic phase was reported Brommer et al. [27] as was already shown in Sect. 6.5.3 in this chapter.

Measurements of forced magneto-strictions and thermal expansions were done by Suzuki and Masuda [34, 35] to check the validity of the MU theory. They showed that the forced magneto-volume coupling constant C decreases with increasing temperature, according to the $T^{4/3}$-linear dependence [34, 35]. In their analysis they assume the presence of the following thermal expansion from the nonmagnetic origin:

$$\alpha_{nm} = aT + bT^3,$$

where the second term results from the lattice vibrations. In the paramagnetic phase at high temperatures, they extract the magnetic contribution by subtracting the Debye part. They concluded that the magneto-volume thermal expansion is present even in the paramagnetic phase that tends to saturate with increasing temperature.

$ZrZn_2$

The forced magneto-striction of this compounds was reported by Ogawa and Waki [36] as given by

$$\omega = 1.02 \times 10^{-10} M^2, \ (M \text{ in emu/mole}),$$

based on their measurements over the temperature range from 4.2 to 40 K under the external field up to 10 kOe. Around the same time, Meincke et al. [37] also reported their measurements of the thermal expansion $\omega(T)$ in the range up to 6.8 K, and the forced magneto-volume striction at 4.2 K under the external field up to 35 kOe. Their results are summarized by

$$\omega(T) = -10.6 \times 10^{-8}\, T^2, \quad \omega = 1.80 \times 10^{-10} M^2, \ (M \text{ in emu/mole}).$$

There exists almost two times difference between the above forced magneto-volume coupling constants.

As for the pressure effect on T_c, Wayne and Edwards [38] reported the value, $-1.95\,\text{K kbar}^{-1}$, for samples with $T_c = 21.5\,\text{K}$. Then nearly the same pressure decrease of the critical temperature, $T_c = 22.2 - 1.9P\,\text{K}$ (P in units of kbar), was later reported by Smith [39] under the pressure up to 25 kbar. A slightly different $\mathrm{d}T_c/\mathrm{d}p = -1.29$ K/kbar ($T_c = 27.6\,\text{K}$) was also reported by Huber et al. [40].

MnSi

The results of measurements of the thermal volume expansion and the forced magneto-striction were reported by Fawcett et al. [41]. According to them, $\partial\sigma/\partial\omega = 8.5$ was obtained as a volume dependence of the spontaneous magnetization. Bloch et al. [42] reported the values, $\mathrm{d}\log M/\mathrm{d}p = -1.15 \times 10^{-2}\,\text{kbar}^{-1}$ and $\mathrm{d}\log T_c/\mathrm{d}p = -3.9 \times 10^{-2}\,\text{kbar}^{-1}$, as the pressure dependence of the spontaneous magnetization at 4.2 K and the pressure effect on T_c, respectively. They amount to $\mathrm{d}\log M/\mathrm{d}\omega = 16$ and $\mathrm{d}\log T_c/\mathrm{d}\omega = 53$, if the observed value of the compressibility $\kappa^{-1} = -1.36 \times 10^6\,\text{kbar}^{-1}$ is used. Thessieu et al. [43] also independently measured the pressure dependence of $M_0(0)$ and T_c, and estimated the pressure dependence of spectral parameters T_0 and T_A. The pressure effect on both $M_0(0)$ and T_c are also reported by Koyama et al. [44], recently.

Meanwhile, the temperature dependence of the magneto-volume expansion and the forced magneto-striction were measured by Matsunaga et al. [6] up to the temperature 200 K for the purpose to confirm the prediction of the MU theory. They reported the following value as the coupling constant of the forced striction at 4.2 K.

$$\omega = 1.49 \times 10^{-10} M^2, \quad (M \text{ in emu/mole})$$

As its temperature dependence, values $\rho\kappa C = 10.25$, 5.88, 5.63, and 6.08×10^{-7} (g/emu)^2 are estimated at temperatures, $T = 4.2$, 29, 40, and 50 K, respectively. The critical temperature of this compound is around 30 K. On the other hand, the observed coupling constant of the thermal expansion is given by $\rho\kappa C_T = 6.33 \times 10^{-7}$ (g/emu)^2. They also concluded that there exists a definite component of the thermal expansion in the paramagnetic phase other than the effect of lattice vibrations.

Sc_3In

As the pressure effect on the Curie temperature, $\mathrm{d}T_c/\mathrm{d}p = 0.19\,\text{kbar}^{-1}$ ($\mathrm{d}\log T_c/\mathrm{d}\omega = -13$) was estimated by Gardner et al. [45] for sample with $T_c = 6.1$ K. Later, Grewe et al. [46] made the same experiments under the pressure up to 6 kbar by applying the magnetic field up to 57 kOe in the range of temperature from 3 to 300 K. The pressure dependence of their report is shown below.

$$\frac{\mathrm{d}T_c}{\mathrm{d}p} = \begin{cases} 0.15 \ \ (\mathrm{K/kbar}), & T_c = 5.5\mathrm{K}, \ \text{for 24.1 at \% In} \\ 0.195 \ \ (\mathrm{K/kbar}), & T_c = 6.0\mathrm{K}, \ \text{for 24.3 at \% In} \end{cases}$$

They correspond to $\mathrm{d}\log T_c/\mathrm{d}p = 2.7$, and 3.25 % kbar^{-1}, respectively. As the pressure effect on the spontaneous magnetization at 3 K for the same. In concentrations, $\mathrm{d}\log M_0/\mathrm{d}p = 0.85$, 0.94 % kbar^{-1} were reported.

$Y(Co,Al)_2$

The Al-substituted Laves phase compounds $Y(Co_{1-x}Al_x)_2$ have attracted much interest since they show metamagnetic transitions. The magneto-volume effect of this compound with $x \sim 0.15$ was measured by Armitage et al. [47]. They reported the values, $\mathrm{d}\log T_c/\mathrm{d}\omega = \mathrm{d}\log \sigma_0(0)/\mathrm{d}\omega = 120 \pm 17$. Later, the measurements of magnetization, magneto-volume expansion, and magneto-volume striction had been made by Duc et al. [48] in the presence of high magnetic field under the high pressure. In these studies, the value of the compressibility, $\kappa = 9.4 \times 10^{-4}\,(\mathrm{kbar})^{-1}$ in Yamada and Shimizu [49] were used.

Ni-Pt Alloys and Other Compounds

The forced magneto-striction measurements were made by Kortekaas et al. [4] on Ni-Pt alloys (of density $\rho = 17\,\mathrm{g/cm^3}$). According to them, $\rho\kappa C \times 10^6 = 4.50\,(\mathrm{G^{-2}g^2cm^{-6}})$ was obtained as a coupling constant of the alloy at 36.6 at % Ni concentration at 4.2 K. The value decreases with increasing the Ni concentration, reaching the value 3.32 at the concentration, 45.2 at % Ni. These values tend to decrease with increasing temperature. In addition to this, thermal volume expansion measurements on (Fe, Co)Si and YNi_3 were reported by Shimizu et al. [50] and Parviainen, Lehtinen [51], respectively. Oraltay et al. [52] reported their thermal expansion, specific heat, and forced magneto-striction measurements on Y_9Co_7.

Heusler Alloys

Recently, the pressure effect on the critical temperature and the spontaneous magnetic moment of ferromagnetic heusler alloys have been measured on Co_2ZrAl by Kanomata et al. [53] and Rh_2NiGe by Adachi et al. [54], for instance.

To summarize, many observations described above show that forced magneto-volume coupling constants are temperature dependent. At first, its dependence was regarded as resulting from the T^2/T_F^2-linear dependence of the SEW theory.

Table 6.1 Grüneisen parameters estimated from the pressure effects on T_c and M_0

Compounds	$-\dfrac{\mathrm{d}\log M_0}{\mathrm{d}p}$	$-\dfrac{\mathrm{d}\log T_c}{\mathrm{d}p}$	$\kappa\gamma_{0A}$	γ_{0A}/γ_m	References
$TiFe_{0.5}Co_{0.5}$	13.8	19.3	1.4	0.051	[55]
$Ni_{75}Al_{25}$	8.7	11.6	1.45	0.083	[33]
$Y(Co_{0.85}Al_{0.15})_2$	120	113	67	0.279	[47]
Co_2ZrAl	1.8	2.2	0.5	0.139	[53]
$Fe_{67}Ni_{33}$	6.9	8.9	1.45	0.105	[56]
$ZrZn_{1.9}$	44	46.7	19.3	0.219	[40]
$Ni_{45}Pt_{55}$	21	18	13.5	0.321	Kanomata[a]
$Fe_{0.3}Co_{0.7}Si$	16	12	12	0.375	[57, 58]
MnSi	12.2	38	−19.7	−0.807	[44]
Co_2TiGa	2.9	9.5	−5.2	−0.897	[59]
$Sc_{75.7}In_{24.3}$	−9.4	−32.5	18.4	−0.979	[46]
Rh_2NiGe	1.5	5.3	−3.1	−1.033	[54]

[a] Private commun.

However, the dependence has soon become of little interest. Results of the pressure effect on the spontaneous magnetic moment and the critical temperature are summarized in Table 6.1. The value of $\kappa\gamma_{0A}$ estimated from (6.116) and its ratio to $\kappa\gamma_m$ are also shown in fourth and fifth columns of the table, respectively. From this table, we will find that the parameters γ_0 and γ_A are not negligible compared to γ_m. According to the SEW theory, values of the second and third columns of this table would be in agreement with each other. Values of the fourth column are assumed to be zero in the MU theory. Experimentally estimated values of this table do seem to support neither of them. In the case of MnSi, for example, the larger suppression of the critical temperature T_c by the external pressure than that of $M_0^2(0)$ can be accounted by neither of them. The problem is easily solved by introducing two new parameters, γ_0 and γ_A.

For confirmation of some mutual correlations among the magnetic Grüneisen parameters, the values of γ_m for magnets in Table 6.1 are plotted against $\gamma_{0,A}$ in Fig. 6.13. No definite correlations seem to be present in the figure. They are all regarded as significant parameters to be used to characterize the magneto-volume effects of itinerant electron magnets.

6.8 Summary of Magneto-Volume Effects

In this chapter, we have shown that the magneto-volume effect is derived from the explicit volume dependence of the free energy that is used in our treatment of the magnetic specific heat in the preceding chapter. It enables our unified understanding of the magneto-volume effect, as well as the thermal and magnetic properties of magnetic susceptibility, magnetic isotherms, and magnetic specific heat. For this

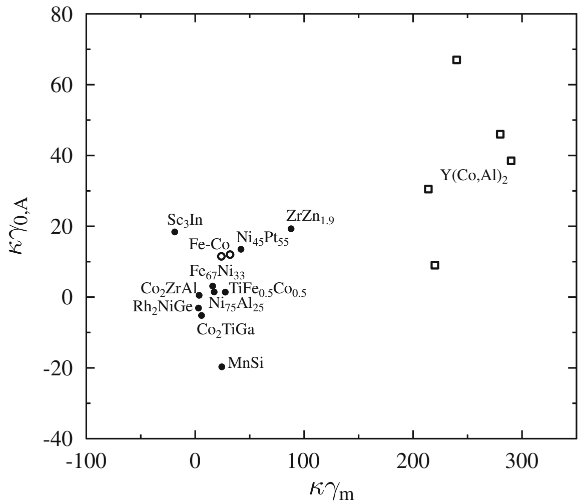

Fig. 6.13 Correlation between Grüneisen parameters, $\gamma_{0,A}$ and γ_m

purpose, three non-traditional magnetic Grüneisen parameters, γ_m, γ_0, and γ_A are introduced, that characterize the interactions between the magnetism and the volume of magnets. As a result, the following novel properties have been derived as summarized below.

- The magneto-volume expansion $\omega_m(t)$ that consists of two kinds of components
  The thermal component $\omega_{th}(t)$, resulting from the finite parameter γ_0, has long been neglected. The presence of this term is evident from the thermodynamic relation between the thermal volume expansion and the magnetic specific heat at low temperatures. The other one, $\omega_{zp}(t)$, related with the parameter γ_m corresponds to the conventional contribution predicted by the SEW and MU theories.
- The new magneto-volume coupling constants defined for the component $\omega_{zp}(t)$
  Two magneto-volume coupling constants C_s and C_h are necessary for spontaneous and forced magneto-strictions, respectively. They have different values ($C_s \sim 2C_h/5$) and are both temperature dependent.
- The anomalous critical forced magneto-striction observed at the critical temperature
  At the critical temperature, the forced magneto-volume expansion $\omega_h(\sigma, t_c)$ becomes proportional to σ^4.
- The revised relation satisfied between $\mathrm{d}\log T_c/\mathrm{d}p$ and $\mathrm{d}\log\sigma_0^2(0)/\mathrm{d}p$
  Because of the presence of multiple Grüneisen parameters, a somewhat different relation is satisfied between the above two pressure effects.

There seem to be many observed magneto-volume measurements that will support the above theoretical predictions.

References

1. T. Moriya, K. Usami, Solid State Commun. **34**, 95 (1980). doi:10.1016/0038-1098(80)91241-7
2. E.P. Wohlfarth, J. Phys. C **2**(2), 68 (1969). doi:10.1088/0022-3719/2/1/309, http://stacks.iop.org/0022-3719/2/68
3. D.L. Mills, Solid State Commun. **9**, 929 (1971). doi:10.1016/0038-1098(71)90515-1
4. T.F.M. Kortekaas, J.J.M. Franse, J. Phys. F: Met. Phys. **6**(6), 1161 (1976). doi:10.1088/0305-4608/6/6/028, http://stacks.iop.org/0305-4608/6/1161
5. V. Heine, Phys. Rev. **153**, 673 (1967). doi:10.1103/PhysRev.153.673, http://link.aps.org/abstract/PR/v153/p673
6. M. Matsunaga, Y. Ishikawa, T. Nakajima, J. Phys. Soc. Jpn. **51**(4), 1153 (1982). doi:10.1143/JPSJ.51.1153, http://jpsj.ipap.jp/link?JPSJ/51/1153/
7. S. Ogawa, Physica B+C **119**(1–2), 68 (1983). doi:10.1016/0378-4363(83)90168-7
8. H. Hasegawa, J. Phys. C: Solid State Phys. **14**, 2793 (1981). doi:10.1088/0022-3719/14/20/017, http://stacks.iop.org/0022-3719/14/2793
9. Y. Kakehashi, J. Phys. Soc. Jpn. **50**(6), 1925 (1981), http://jpsj.ipap.jp/link?JPSJ/50/1925
10. H. Hasegawa, J. Phys. Soc. Jpn. **51**(3), 767 (1982), http://jpsj.ipap.jp/link?JPSJ/51/767
11. H. Hasegawa, M.W. Finnis, D. Pettifor, J. Phys. F **15**, 19 (1985). doi:10.1088/0305-4608/15/1/007, http://stacks.iop.org/0305-4608/15/19
12. H. Hasegawa, Physica B+C **119**, 15 (1983). doi:10.1016/0378-4363(83)90158-4
13. Y. Kakehashi, J. Phys. Soc. Jpn. **49**(5), 1790 (1980). doi:10.1143/JPSJ.49.1790, http://jpsj.ipap.jp/link?JPSJ/49/1790/
14. A.J. Holden, V. Heine, J.H. Samson, J. Phys. F **14**, 1005 (1984). doi:10.1088/0305-4608/14/4/022, http://stacks.iop.org/0305-4608/14/1005
15. R. Joynt, V. Heine, J. Magn. Magn. Mater. **45**, 74 (1984). doi:10.1016/0304-8853(84)90375--5
16. T. Moriya, A. Kawabata, J. Phys. Soc. Jpn. **34**(3), 639 (1973). doi:10.1143/JPSJ.34.639. http://jpsj.ipap.jp/link?JPSJ/34/639/
17. T. Moriya, A. Kawabata, J. Phys. Soc. Jpn. **35**(3), 669 (1973), http://jpsj.ipap.jp/link?JPSJ/35/669
18. D.M. Edwards, C.J. Macdonald, Physica B+C **119**, 25 (1983). doi:10.1016/0378-4363(83)90160-2
19. A.Z. Solontsov, D. Wagner, Phys. Rev. B **51**, 12410 (1995). doi:10.1103/PhysRevB.51.12410, http://link.aps.org/abstract/PRB/v51/p12410
20. Y. Takahashi, H. Nakano, J. Phys.: Condens. Matter **18**(2), 521 (2006). doi:10.1088/0953-8984/18/2/013, http://www.iop.org/EJ/abstract/0953-8984/18/2/013/
21. E. Fawcett, J. Phys.: Condens. Matter **1**, 203 (1989). doi:10.1088/0953-8984/1/1/017, http://stacks.iop.org/0953-8984/1/203
22. S. Kambe, J. Flouquet, P. Lejay, P. Haen, A. de Visser, J. Phys.: Condens. Matter **9**, 4917 (1997). doi:10.1088/0953-8984/9/23/015, http://stacks.iop.org/0953-8984/9/4917
23. T.F.M. Kortekaas, J.J.M. Franse, Hölscher, Phys. Lett. A **48**(4), 305 (1974). doi:10.1016/0375-9601(74)90515-5
24. S. Ogawa, N. Kasai, J. Phys. Soc. Jpn. **27**, 789 (1969). doi:10.1143/JPSJ.27.789, http://jpsj.ipap.jp/link?JPSJ/27/789/
25. G. Creuzet, I.A. Campbell, J.L. Smith, J. Physique Lett. **44**, L-547–L-552 (1983)
26. Y. Takahashi, J. Phys.: Condensed Matter **2**, 8405 (1990). doi:10.1088/0953-8984/2/42/017, http://stacks.iop.org/0953-8984/2/8405
27. P.E. Brommer, G.E. Grechnev, J.J.M. Franse, A.S. Panfilov, Y.Y. Pushkar, I.V. Svechkarev, J. Phys.: Condens. Matter **7**, 3173 (1995). doi:10.1088/0953-8984/7/16/011, http://stacks.iop.org/0953-8984/7/3173
28. J.J.M. Franse, Physica B+C **86–88**, 283 (1977). doi:10.1016/0378-4363(77)90316-3
29. J.J.M. Franse, J. Magn. Magn. Mater. **10**, 259 (1979). doi:10.1016/0304-8853(79)90189--6
30. P.E. Brommer, J.J.M. Franse, J. Magn. Magn. Mater. **45**, 129 (1984). doi:10.1016/0304-8853(84)90386-X

31. P.E. Brommer, J.J.M. Franse, *Feromagnetic Materials*, ed. by K.H.J. Buschow, E.P. Wohlfarth. Strongly Enhanced Itinerant Intermetallics and Alloys, vol. 5 (North-Holland, Amsterdam, 1990)
32. N. Buis, J.J.M. Franse, J.V. Haarst, J. Kaandorp, T. Weesing, Phys. Lett. A **56**(2), 115 (1976). doi:10.1016/0375-9601(76)90164-X
33. N. Buis, J.J.M. Franse, P.E. Brommer, Physica B+C **106**, 1 (1981). doi:10.1016/0378-4363(81)90007-3. (For stoichiometric compound by interpolation)
34. K. Suzuki, Y. Masuda, J. Phys. Soc. Jpn. **54**(2), 630 (1985), http://jpsj.ipap.jp/link?JPSJ/54/630
35. K. Suzuki, Y. Masuda, J. Phys. Soc. Jpn. **54**(1), 326 (1985), http://jpsj.ipap.jp/link?JPSJ/54/326
36. S. Ogawa, S. Waki, J. Phys. Soc. Jpn. **22**(6), 1514 (1967). doi:10.1143/JPSJ.22.1514, http://jpsj.ipap.jp/link?JPSJ/22/1514
37. P.P.M. Meincke, E. Fawcett, G.S. Knapp, Solid State Commun. **7**, 1643 (1969). doi:10.1016/0038-1098(69)90046-5
38. R.C. Wayne, L.R. Edwards, Phys. Rev. 188(2), 1042 (1969).10.1103/PhysRev.188.1042. http://link.aps.org/abstract/PR/v188/p1042
39. T.F. Smith, J.A. Mydosh, E.P. Wohlfarth, Phys. Rev. Lett. **27**(25), 1732 (1971). doi:10.1103/PhysRevLett.27.1732, http://link.aps.org/abstract/PRL/v27/p1732
40. J.G. Huber, M.B. Maple, D. Wohlleben, Solid State Commun. **16**, 211 (1975). doi:10.1016/0038-1098(75)90577-3
41. E. Fawcett, J.P. Maita, J.H. Wernick, Intern. J. Magn. **1**, 29 (1970)
42. D. Bloch, J. Voiron, V. Jaccarino, J.H. Wernick, Phys. Lett. A **51**(5), 259 (1975). doi:10.1016/0375-9601(75)90438-7
43. C. Thessieu, K. Kamishima, T. Goto, G. Lapertot, J. Phys. Soc. Jpn. **67**(10), 3605 (1998). doi:10.1143/JPSJ/67.3605, http://jpsj.ipap.jp/link?JPSJ/67/3605/
44. K. Koyama, T. Goto, T. Kanomata, R. Note, Phys. Rev. B **62**(2), 986 (2000). doi:10.1103/PhysRevB.62.986, http://link.aps.org/abstract/PRB/v62/p986
45. W.E. Gardner, T.F. Smith, B.W. Howlett, C.W. Chu, A. Sweedler, Phys. Rev. **166**(2), 577 (1968). doi:10.1103/PhysRev.166.577, http://link.aps.org/abstract/PR/v166/p577
46. J. Grewe, J.S. Schilling, K. Ikeda, K.A.J. Gschneidner, Phys. Rev. B **40**(13), 9017 (1989). doi:10.1103/PhysRevB.40.9017, http://link.aps.org/abstract/PRB/v40/p9017
47. J.G. Armitage, R.G. Graham, P.C. Riedi, J.S. Abell, J. Phys.: Condens. Matter 2, 8779 (1990). doi:10.1088/0953-8984/2/44/007, http://stacks.iop.org/0953-8984/2/8779
48. N.H. Duc, J. Voiron, S. Holtmeier, P. Haen, X. Li, J. Magn. Magn. Mater. **125**, 323 (1993). doi:10.1016/0304-8853(93)90106-C
49. H. Yamada, M. Shimizu, J. Phys.: Condens. Matter **1**, 2597 (1989). doi:10.1088/0953-8984/1/15/006, http://stacks.iop.org/0953-8984/1/2597
50. K. Shimizu, H. Maruyama, H. Yamazaki, H. Watanabe, J. Phys. Soc. Jpn. **59**(1), 305 (1990), http://jpsj.ipap.jp/link?JPSJ/59/305
51. S. Parviainen, M. Lehtinen, J. Magn. Magn. Mater. **30**, 87 (1982). doi:10.1016/0304-8853(82)90012-9
52. R.G. Oraltay, J.J.M. Franse, P. Brommer, A. Menovsky, J. Phys. F **14**, 737 (1984). doi:10.1088/0305-4608/14/3/019, http://stacks.iop.org/0305-4608/14/737
53. T. Kanomata, T. Sasaki, H. Nishihara, H. Yoshida, T. Kaneko, S. Hane, T. Goto, N. Takeishi, S. Ishida, J. Alloy Compd. **393**(1–2), 26 (2005). doi:10.1016/j.jallcom.2004.09.071
54. Y. Adachi, H. Morita, T. Kanomata, H. Yanagihashi, H. Yoshida, T. Kaneko, H. Fukumoto, H. Nishihara, M. Yamada, T. Goto, J. Alloys Compd. **419**(1–2), 7 (2006). doi:10.1016/j.jallcom.2005.09.066
55. J. Beille, D. Bloch, F. Towfiq, Solid State Commun. **25**(2), 57 (1978). doi:10.1016/0038-1098(78)90355-1
56. M. Shiga, *Invar Alloys*, vol. 3B (VHC, Weinheim, 1994)
57. J. Beille, D. Bloch, F. Towfiq, J. Voiron, J. Magn. Magn. Mater. **10**(2–3), 265 (1979). doi:10.1016/0304-8853(79)90190-2
58. K. Miura, M. Ishizuka, T. Kanomata, H. Nishihara, F. Ono, S. Endo, J. Magn. Magn. Mater. **305**(1), 202 (2006). doi:10.1016/j.jmmm.2005.12.016
59. T. Sasaki, T. Kanomata, T. Narita, H. Nishihara, R. Note, H. Yoshida, T. Kaneko, J Alloy Compd. **317–318**, 406 (2001). doi:10.1016/S0925-8388(00)01417-1