Journal of the Physical Society of Japan
vo1. 50, No. 8, August, 1981, pp. 2573-2580

Magnetovolume Effects in Ferromagnetic Transition Metals

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(Received March 10, 1981)

Magnetovolume effects in ferromagnetic transition metals and alloys, such as the spontaneous volume magnetostriction, the forced volume magnetostriction, are described by a phenomenological theory based upon a fluctuating local band picture, in which both itinerant electron and local moment characters are taken into account. The magnetovolume effects of Fe, Ni and the Fe-Ni Invar alloy are analyzed on the basis of the proposed theory. It has been shown that the degree of shrinkage of local moments above the Curie temperature can be estimated from this analysis. It is concluded that local moments remain almost unchanged in bcc Fe and, on the contrary, they shrink markedly in the Invar alloy.

§ 1.Introduction

Magnetovolume effects in ferromagnetic transition metals such as the volume magnetostriction and the pressure effects on both magnetization and Curie temperature give us fruitful information on the basic problems of magnetism of metals and alloys.[1] so far, these effects have been treated theoretically in the frameworks of two extreme models, namely the local moment model and the itinerant electron model. The most conventional treatment is based upon the local moment model or the Heisenberg model. An elegant theory has been developed by Callen and Callen in this framework.[2] The volume change due to magnetic coupling, ω, is given by the two spin correlation function <$\boldsymbol{m}_i \cdot \boldsymbol{m}_j$>) as:

$$\omega = \kappa \sum_{i,j} C^{\text{int}} \left\langle \vec{m}_i \cdot \vec{m}_j \right\rangle, \qquad (1)$$

where κ is the compressibility, C^{int} the magnetovolume coupling constant originated in the volume dependence of exchange integral and *i*, *j* are lattice sites.

It is now obvious that 3*d* electrons in metals form the energy band with the width of a few eV. Therefore, magnetovolume effects should be also explained by an itinerant electron model. It has been pointed out that the atomic distance dependence of the band width could cause magnetovolume effects.[3] Andersen *et al*. have correctly estimated the pressure effect on the magnetization at 0 K, dM/dP for bcc Fe based upon the band theory.[4] The spontaneous volume magnetostriction, ω_s, can be explained as follows: The band polarization causes an increase in the kinetic energy. The cost of the kinetic energy can be saved by a volume expansion because the 3*d* band width *W* is highly dependent on the atomic separation *R*, like $W \propto R^{-5}$.[5] The increase in the kinetic energy is proportional to the square of magnetization *M* in the first approximation. Therefore, the volume change due to the band polarization may be given by,

$$\omega = \kappa C^{\text{band}} M^2, \qquad (2)$$

where C^{band} is the magnetovolume coupling constant due to the present mechanism. Recent self-consistent spin-polarized energy band calculations have shown a large volume expansion of several percent for Fe.[6] However, such a large volume change has not been observed for Fe. An apparent lack of this giant volume change expected from the band calculation might be explained as that the effective 3*d* band splitting does not change at T_c. This implies that the Stoner model is inadequate, at least, to describe the ferromagnetism of Fe.

On the other hand, by analyzing the lattice constant of binary alloys of Fe such as Fe-V, Fe-Al and Fe-Co,[7] we have shown that the lattice constant of hypothetical nonmagnetic bcc Fe is smaller than that of ferromagnetic Fe by about 3% as expected from band calculations. These observations lead to a consideration that the spontaneous volume magnetostriction associated with the 3*d* band polarization should be proportional to the square of local moment instead of the bulk magnetization, namely,

$$\omega_s = \kappa C^{band} N \sum_i m_i^2, \qquad (3)$$

where m_i represents the local moment at the site i and N, the number of atoms per unit volume, is multiplied to keep the same definition of κC^{band} as eq. (2).

It is well known that the ground state properties of 3*d* transition metal ferromagnets are well described by a band model but a simple band theory, i.e., the Stoner model fails to explain many experimental facts at high temperatures. For example, the band theory gives a correct estimate of dM/dP in bcc Fe at 0 K but fails to explain the lack of giant spontaneous volume magnetostriction. Many approaches have been made to get more realistic understandings of the high temperature properties by taking into account of the effect of spin fluctuations8) or local moment characters.[9] In this paper, we present a unified model in which both local and itinerant characters are taken into account and develop a phenomenological theory of magnetovolume effects for ferromagnetic transition metals.

§ 2. Phenomenological Theory

First, we present a simple picture of a metallic ferromagnet by introducing the concept of a flexible local moment. A schematic picture of this model is shown in Fig. 1. It is assumed that a magnetic moment is localized at each atomic site and the behavior of each local moment is described by the Stoner model and hence the magnitude of the local moment can be changed by applying an external field or by raising temperature. The z axis of each band is different site by site. A theory which justifies such a local band picture has been developed by Korenman *et al.*[9] we treat these quasi-local moments as classical local moments hereafter.

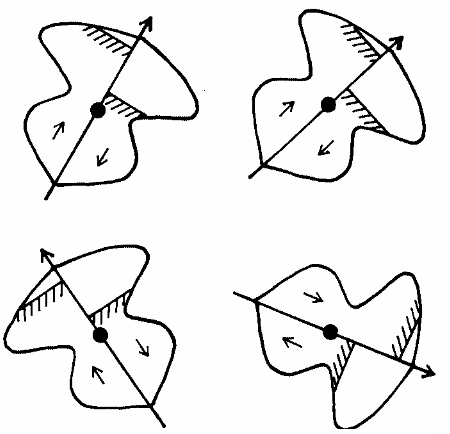

Fig. 1. Schematic picture of the local band model.

2.1 Magnetization

Defining the local moment at the site i under the applied field H and the temperature T as $m_i(H, T)$, we may write the bulk magnetization as,

$$M(H,T) = \sum_i m_i(H,T)\cos\theta_i \qquad (4)$$

where θ_i means the angle between the applied field and the direction of the local moment m_i. Considering a pure metal and neglecting the fluctuation of magnitude of m_i (longitudinal spin fluctuation), eq. (4) can be written as:

$$M(H,T) = N\int \rho_{H,T}(\theta)\cdot m(H,T,\theta)\cdot \cos\theta \, d\Omega \qquad (5)$$

where $\rho_{H,T}(\theta)$ is the angular distribution function of the local moment, which depends on the applied field H and the temperature T. N represents the number of atoms per unit volume. The magnitude of local moment may increase or decrease by applying an external field. From symmetry considerations, the change in the magnitude of a local moment, Δm, may be given by

$$\Delta m = \chi_l H \cos\theta / N, \qquad (6)$$

where χ_l is the susceptibility of the local band. Therefore, we have

$$m(H,T,\theta) = m(0,T,\theta) + \chi_l H \cos\theta / N. \qquad (7)$$

Noting that the magnitude of m does not depend on θ without an external field, we may write simply

$$m = m_0 + \Delta m = m_0 + \chi_l H \cos\theta / N \qquad (7')$$

At 0 K, where all moments align parallel to the applied field, χ_l is equal to the Stoner susceptibility, χ_{st}. According to the original Stoner theory, χ_{st} should diverge at T_c. However, recent band calculations indicate that the divergence of χ_{st} should take place at a much higher temperature than the actual T_c.[10] It seems more likely that the Stoner theory describes the behavior of local bands. Then, we may regard the calculated χ_{st}, which is weakly temperature dependent at least below T_c, as χ_l.

2.2 Volume change

As described in a previous section, the correlation between the volume change and the local magnetic moment may be given by the sum of two contributions, namely, the volume change caused by a change in the magnitude of local moments and that caused by a change in relative orientations of neighboring local moments, as given by the following equation,

$$\omega = \kappa\left[C^{band}N\sum_i m_i^2 + C^{\text{int}}\sum_{i,j}\left\langle \vec{m}_i \vec{m}_j\right\rangle_{T,H}\right], \quad (8)$$

where C^{band} and C^{int} are the coupling constants between the volume and the magnetic moment in each term. Since the first term originates in the increase of the kinetic energy due to polarization of local bands, we call this term the band term, whereas the second term expressed by the correlation function $\langle \boldsymbol{m}_i \boldsymbol{m}_j \rangle$, is called the interaction term because it represents magnetic interactions between neighboring local moments. For pure metals, eq. (8) can be rewritten as:

$$\omega = \kappa\left[C^{band}N^2\int \rho(\theta)m^2 d\Omega + C^{\text{int}}\sum_{i,j}\left\langle \vec{m}_i \vec{m}_j\right\rangle\right] \quad (9)$$

Band calculations for pure metals predict a large (a few percent) contribution of the band term if a local moment of 1～2 μ_B really vanished above T_c.[6] In alloys, m_l usually varies with concentration. The deviation of the lattice constant from Vegard's law[7,11] in magnetic alloys of transition metals may be ascribed to the band term.

On the other hand, it is a fundamental problem of magnetism of metals whether the magnitude of local moments decreases with increasing temperature. In order to know the temperature dependence of local moment from the temperature dependence of the spontaneous volume magnetostriction, it is necessary to estimate the contribution of the interaction term. Kanamori and Teraoka[12] have introduced a theory of magnetovolume effects in an interacting local moments system based upon the Alexander-Anderson-Moriya model.[13,14] However, it is difficult to estimate the interaction term in particular metal from their theory because it sensitively depends on details of the band shape near the Fermi energy. In this paper, we will show that these two contributions can experimentally be separated by analyzing the magnetovolume effect, i.e., the forced volume magnetostriction, and hence we can get an answer to the fundamental problem in the framework of the present theory.

a) *Spontaneous volume magnetostriction*

The spontaneous volume magnetostriction, ω_s, is the volume change accompanied with the onset of spontaneous magnetization. Thermodynamically, it is defined as the difference between the volume thermal expansion at a constant field, H=0, and at a constant magnetization, M=0. Experimentally, it is usually obtained by subtracting the thermal expansion due to unharmonic lattice vibrations, which may be estimated by assuming a Debye solid, from the observed thermal expansion. On the other hand, eq. (9) gives the volume change from the completely nonmagnetic state, namely m_i=0 for all i, and hence is not equivalent to ω_s. In terms of ω given by eq. (9), ωs should be defined as

$$\omega_s(T) = \omega(T) - \omega(T >> T_c)\big|_{H=0} = N^2\kappa\left[C^{band}\left\{m_0(T)^2 - m_0(T >> T_C)^2\right\} + C^{\text{int}}\left\langle \overline{\vec{m}_i \vec{m}_j}\right\rangle\right] \quad (10)$$

where $m_0(T)$ means the magnitude of local moment at the temperature T without an applied field. Since $N^2\langle \boldsymbol{m}_i \boldsymbol{m}_j \rangle$ may be approximated by $M_s(T)^2$ except near T_c, we have

$$\varpi_s = \kappa\left[N^2 C^{band}\left\{m_0(T)^2 - m_0(T >> T_C)^2\right\} + C^{\text{int}} M_s(T)^2\right], \quad (11)$$

For a Heisenberg ferromagnet, only the second term is responsible to ω_s, which may be given by[15]

$$\omega_s = \frac{z}{Ng^2\mu_B^2}\frac{dJ}{d\omega}M_s(T)^2, \quad (12)$$

therefore

$$C^{\text{int}} = \frac{z}{Ng^2\mu_B^2}\cdot\frac{dJ}{d\omega}$$

where $dJ/d\omega$ is the volume derivative of the exchange integral and other notations are conventional ones.

As discussed previously, the coupling constant C^{band} should be fairly large positive; probably the order of $\kappa C^{\mathrm{band}} = 10^{-8}$ $\mathrm{cm}^6/\mathrm{emu}^2$. Therefore, if a shrinkage of local moments really takes place with increasing temperature, a large ω_s should be observed. A large ω_s observed in $R\mathrm{Co}_2$ intermetallic compounds, in which Co sublattice is considered to behave as a Stoner ferromagnet, may be an example of this case.[16,17] However, if the magnitude of local moments does not change with temperature, the first term does not contribute to ω_s. Once the contribution of the second term is estimated by some methods, then we can get information about the change in the magnitude of local moments by analyzing the thermal expansion of ferromagnetic metals and alloys.

b) *Forced volume magnetostriction*

When an external field is applied, the magnitude of local moments changes following eq. (7) and, at the same time, the correlation function $\langle \boldsymbol{m}_i \boldsymbol{m}_j \rangle_T$ increases leading to a change in volume. This change in volume is called the volume magnetostriction, ω_H. First, let us examine the contribution of the band term. Noting eq. (7), we have an equation

$$m^2 = (m_0 + \Delta m)^2 = m_0^2 + \frac{2\chi_l H}{N} m_0 \cos\theta + \frac{\chi_l^2 H^2}{N^2} \cos^2\theta \tag{13}$$

Putting this equation into eq. (9), we have

$$\begin{aligned} \omega_H^{band} &= \kappa C^{band}\left[N^2 m_0^2 + 2N\chi_l H \int \rho(\theta)(m_0 + \Delta m)\cos\theta\, d\Omega - \chi_l^2 H^2 \int \rho(\theta)\cos^2\theta\, d\Omega\right] \\ &= \kappa C^{band}\left[Const. + 2\chi_l H\, M(H,T) - A\chi_l^2 H^2\right] \end{aligned} \tag{14}$$

where the relations $\int\rho(\theta)d\Omega=1$ and $A=\int\rho(\theta)\cos^2\theta d\Omega$ as well as eq. (5) are used. A is a constant ranging $⅓\le A\le 1$. For a usual ferromagnet, $M \gg \chi_l H$ and hence the final term of eq. (14) may be neglected. Then we have

$$\omega_H^{band} = 2\kappa C^{band}\chi_l H\, M(H,T) + Const. \tag{15}$$

Differenciating eq. (15) by H, we have the forced volume magnetostriction $d\omega/dH$,

$$\left(\frac{d\omega}{dH}\right)^{band} = 2\kappa C^{band}\left[\chi_l M(H,T)) + \chi_l H\frac{dM}{dH}\right] \approx 2\kappa C^{band}\chi_l M(H,T), \tag{16}$$

where the small term involving the square of susceptibility is again neglected in the final formula.

The contribution of the interaction term to ω_H is described by the localized model provided the change in m_o is not taken into consideration. Such a theory has been developed by several authors[2,15,18] we now only concern with the $d\omega/dH$ below T_c, where the correlation function is approximately proportional to the square of magnetization, namely $N^2\langle \boldsymbol{m}_i \boldsymbol{m}_j\rangle = M(H,T)^2$. Then we have

$$\left(\frac{d\omega}{dH}\right)^{\mathrm{int}} = 2\kappa C^{\mathrm{int}} M(H,T)\frac{dM}{dH}. \tag{17}$$

If we do not consider the change in the magnitude of local moments, dM/dH is attributed to the rotation of local moments and corresponds to the spin wave susceptibility χ_{sw}. However, the interaction term is affected by the change in the magnitude of m_i. The contribution of this effect (the cross term) to $d\omega/dH$ may be given as:

$$\left(\frac{d\omega}{dH}\right)^{cross} = 2\kappa C^{\mathrm{int}} M(H,T)\chi_l \left\langle\overline{\cos\theta_{ij}}\right\rangle \tag{18}$$

where $\left\langle\overline{\cos\theta_{ij}}\right\rangle$ means the reduced correlation function, $\left\langle\overline{m_i m_j}\right\rangle / m^2$. This term may be included in the band term, since it is proportional to $\chi_l M(H, T)$. As will be shown later, C^{int} is much smaller than C^{band} and hence we can approximately describe $d\omega/dH$ as:

$$\frac{d\omega}{dH} = \left(\frac{d\omega}{dH}\right)^{band} + \left(\frac{d\omega}{dH}\right)^{\mathrm{int}} = 2M(H,T)\left[\kappa C^{band}\chi_l + \kappa C^{\mathrm{int}}\chi_{SW}\right] \qquad (19)$$

In a subsequent section, magnetovolume effects are analyzed for some special cases based upon eqs. (11) and (19).

§3. Analyses of Magnetovolume Effects and Discussion

3.1 Local moment limit

In this section, we consider the magnetovolume effects in a local moment system where the magnitude of local moments remains unchanged up to the Curie temperature. Figure 2 represent schematically the temperature dependence of the bulk magnetization $M_s(T)$, the magnitude of local moment m_0, the spin wave susceptibility χ_{sw} and the single particle (Stoner) susceptibility of local band χ_l. In this local moment limit, the decrease in bulk magnetization is ascribed to rotation of local moments or, in other words, to spin wave excitations. Since the degree of polarization of local bands does not change and, of course, the Fermi temperature of the 3*d* band is much higher than T_c, the Stoner susceptibility hardly changes up to T_c. On the other hand, the spin wave susceptibility, which is absent at 0 K, increases with temperature and diverges at T_c.

a) *bcc iron*

For bcc Fe, many data are available to analyze the contributions of χ_{sw} and χ_l. At 0 K, the high field susceptibility χ_{hf} mainly consists of the orbital susceptibility and the Stoner susceptibility χ_{st}, which is, we consider, equal to χ_l. There are several estimates of χ_{st} from band calculations. We employ the value estimated by Foner *et al.*,[19)] i.e. $\chi_l = 2 \times 10^{-5}$ emu/cm^3. Assuming that the orbital moment does not cause a volume change, we can estimate κC^{band} from eq. (16) by using the observed value of $d\omega/dH = 5\times10^{-10}$/Oe at 4.2 K[20)] as $\kappa C^{band} = 0.7\times10^{-8}$ cm^6/emu^2. At room temperature, χ_{hf} increases almost twice.[19)] This increase may be ascribed to χ_{sw}. On the contrary, $d\omega/dH$ does not change within the experimental accuracy.[20)] This means that the contribution of the interaction term to volume change should be very small, that is $C^{band} \gg C^{\mathrm{int}}$.

It is an interesting problem to analyze the spontaneous volume magnetostriction. There are a few data on thermal expansion of bcc Fe which are inconsistent each other.[21-24)] Some of them give a deep dip ($\varDelta\alpha_m$) in thermal expansion coefficient curve ($\alpha(T)$) at Tc.[22,23)] Noting the Ehrenfest relation for the second order phase transition, namely $dT_c/dP = VT_c(3\varDelta\alpha_m/\varDelta C)$, $3\varDelta\alpha_m$, which is the temperature derivative of ω_s at T_c, is thermodynamically related with dT_c/dP. The observed value of dT_c/dP for Fe is nearly zero implying a very small $\varDelta\alpha_m$ contrary to some of the experimental results. We have remeasured the thermal expansion of Fe very carefully, in particular near T_c. The result is shown in Fig. 3, which is in a fairly good agreement with one of recent experimental results.[24)] In both measurements, a small negative dip has been observed at T_c, which means a very small volume expansion below T_c. Putting the pre-

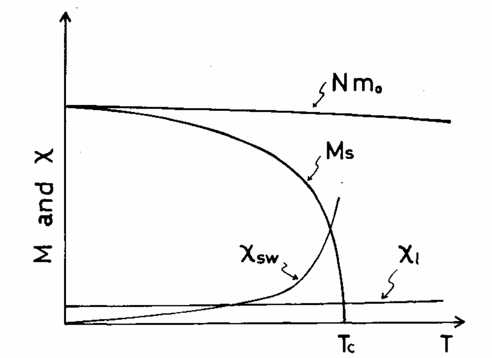

Fig. 2. Temperature dependence of the spontaneous magnetization, M_s, the magnitude of local moment, m_0, and the local band- and spin wave susceptibilities, χ_l and χ_{sw} in a local moment system.

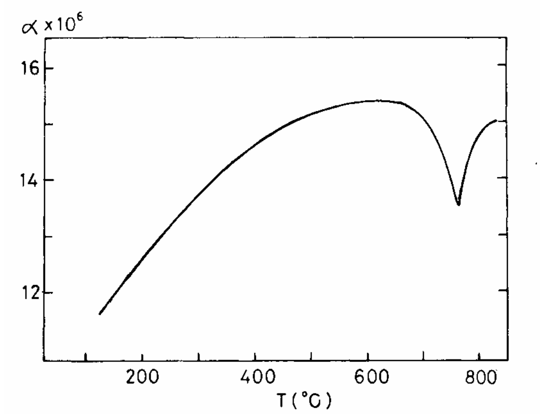

Fig. 3. Temperature dependence of the thermal expansion coefficient of Fe.

sent result of $\Delta\alpha_m$ and ΔC into the Ehrenfest relation, we have dT_c/dP= -0.05 K/kbar. No pressure effect on T_c has been detected by direct measurements within the experimental accuracy.[25,26] our estimated value is within the range of scattering of experimental values of T_c as a function of pressure[26] and hence not inconsistent with the result of dT_c/dP. From our result, ω_s is estimated as, at most, 8×10^{-4} at $0.8T_c$.

Assuming $\omega_s \propto M_s^2$ down -to 0 K, we have estimated ω_{s0} (ω_s at 0 K) as 14×10^{-4}. From the condition $C^{band}>>C^{int}$, we can ascribe ω_s only to the band term. Then we can estimate the shrinkage of m_o from eq. (11) by putting $m_o(T=0)=2.22\ \mu_B$.

$$\omega_s=14\times10^{-4}$$
$$=N^2\kappa C^{band}[(2.22\mu_B)^2-m_0(T>>T_c)^2]. \quad (20)$$

Using $\kappa C^{band}=0.7\times10^{-8}$ cm^6/emu^2, we obtain $m_0(T>>T_c)=2.1\ \mu_B$. However, this is a roughly estimated value because the contribution of the interaction term to ω_s can not be completely negligible for such a small ω_s. It may be concluded that the change in the magnitude of local moment is not more than a few percent. This conclusion seems to be consistent with recent theoretical estimates.[27,28)]

b) Nickel

In a naive band picture, Ni is considered as a strong ferromagnet and hence the 3*d* band susceptibility should be 0 at 0 K. However, taking the *s-d* hybridization into consideration, we may expect a small contribution of χ_{st}. A theoretical calculation of χ_{st} gives 0.8 x 10^{-5} emu/cm^3,[29] which is about a half of the observed susceptibility χ_{hf}= 1.7 x 10^{-5}.[19] putting the experimental value of 1.2×10^{-10} of $d\omega/dH$ at 4.2 K[30] into eq. (l6), we obtain κC^{band}=1.4x 10^{-8} cm^6/emu^2, which is comparable to that of Fe. A distinct feature of $d\omega/dH$ of Ni is its characteristic temperature dependence, namely $d\omega/dH$ changes its sign around 0.7 T_c and becomes negative at high temperatures.[30] This behavior has been interpreted, so far, as a result of competitive contributions of the *s-d* electron transfer and the band width effect to the volume magnetostriction.[31] The former is positive and dominant at lower temperatures and the latter is negative and become larger at higher temperatures. The observed negative $d\omega/dH$ at high temperature is simply explained by the present theory if a negative C^{int} is assumed, because χ_{sw} becomes dominant at high temperatures. The dotted line in Fig. 4 shows the calculated $d\omega/dH$ on the basis of the present

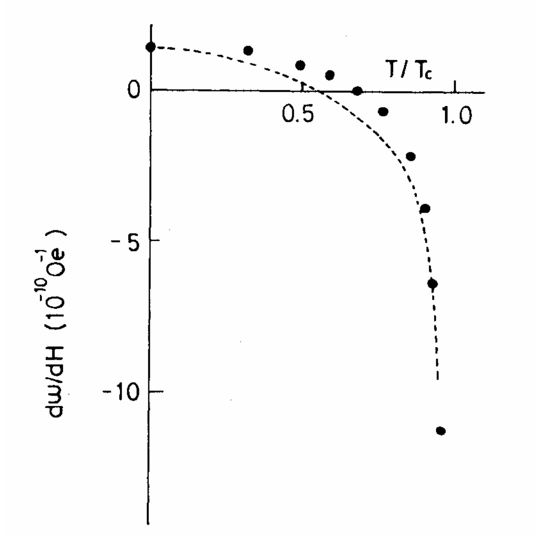

Fig. 4. Temperature dependence of the forced volume magnetostriction, $d\omega/dH$, of Ni. The dotted curve represents the calculated values.

model for the local moment limit assuming that χ_l is constant up to T_c and hence the temperature dependence of χ_{hf}[32] is fully ascribed to χ_{sw}. Here, κC^{int} is adjusted to get the best agreement with experimental results.

3.2 Intermediate state - Invar alloy

It is now believed that the complete collapse of local moments above T_c, as the Stoner theory predicts, is rather unrealistic picture for 3*d* metal ferromagnets. However, the degree of the spin polarization or the magnitude of local moments would decrease in some extent with increasing temperature. If the decrease is appreciable, a notable shrinkage of volume would be expected through the band term in eq. (11). By analyzing the lattice constant of Fe-Ni alloys, we have shown that the large spontaneous volume magnetostriction of the Fe-Ni Invar alloy may be attributable to a shrinkage in the magnitude of local moments.[7,11] Figure 5 shows a schematic diagram of this case. Some of the characteristic properties of the Fe-Ni Invar alloy are the large high field susceptibility, χ_{hf}= 19.7 x 10^{-5} emu/cm^3,[33] and the large $d\omega/dH$ of 75×10^{-10}/ Oe at 4.2K.[34] Ascribing χ_{hf} to $\chi_l=\chi_{st}$, We obtain κC^{band}= 1.4x 10^{-8} cm^6/emu^2, which is almost the same as that of Ni. Thus, the large $d\omega/dH$ at 4.2 K should be ascribed to the large χ_{st} due to weak itinerant ferromagnetism of this alloy. By raising temperature, both χ_{hf} and $d\omega/dH$ increase. From the

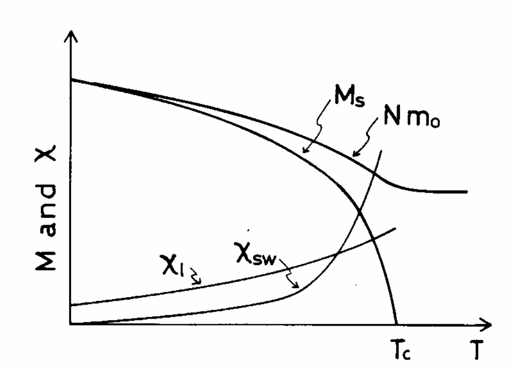

Fig. 5. Temperature dependence of the spontaneous magnetization, M_s, the magnitude of local moment, m_o, and local band- and spin wave susceptibilities, χ_l and χ_{sw} in an intermediate system - Invar alloy.

spin wave stiffness constant obtained from neutron scattering experiments[35] we can estimate the contribution of χ_{sw} to χ_{hf}; D=110meVÅ^2 at 300K, then we have χ_{sw}=20x 10^{-5} at H=5 T. The difference between the observed χ_{hf} (=70x10^{-5}) and χ_{sw}, that is 50x10^{-5}, should be ascribed to χ_l. Therefore, the temperature dependence of χ_l in this case is also notable. Using κC^{band}=1.4x 10^{-8} cm^6/emu^2, we can estimate the band term contribution to $d\omega/dH$ as 150x10^{-10}, which is slightly larger than the observed value, 140x 10^{-10} [34], implying a small negative value of κC^{int}.

The most striking character of the Invar alloy is its large ω_{st}[36] In the present model, the band term should be responsible for this giant ω_s and hence mo should appreciably decrease as shown in Fig. 5. Collins[37] has determined the temperature dependence of the Fe local moment by neutron scattering experiments. According to him, m_{Fe} is roughly 1.4 μ_B above Tc and and 2.3μ_B at 300K. Putting these values into eq. (11) and neglecting the contribution from Ni, we have ω_s(300 K)= 1.3 x 10^{-2}, which is comparable to the observed value, ω_s(4.2K)=1.9x 10^{-2}. Therefore, we may conclude that the large spontaneous volume magnetostriction of the Invar alloy may be ascribed to the shrinkage of local moments with increasing temperature.

3.3 Stoner limit - very weak itinerant electron ferromagnets

If we neglect the effects of rotation of local moments on both the magnetization and the volume change, the present model becomes equivalent to the Stoner model. The magnetovolume effects of Stoner ferromagnets, in particular those of very weak itinerant electron ferromagnets (VWIF), have been intensively studied so far on the basis of the Stoner Edwards-Wohlfarth theory (SEW theory).[38,39] The interrelations between various magnetovolume effects are successfully explained by the SEW theory.[40] Therefore, VWIF can be considered as good examples of Stoner ferromagnets. Recently Moriya and Usami have pointed out, however, an important role of spin fluctuations on magnetovolume effects even in VWIF and reanalyzed the experimental data on the basis of their unified theory of metallic ferromagnets.[41] since the rotation of local moments in our model corresponds to transverse spin fluctuations, it would be possible to treat the magnetovolume effects of VWIF by the present model. We believe that eqs. (9) and (11) would be applicable to VWIF. However, approximations made for getting eq. (19), for instances, disregard of the H^2 term in eq. (14) as well as the ($d\omega/dH$) cross term in eq. (18), may not be correct in this case. Therefore, another treatment is necessary to analyze the magnetovolume effects of VWIF.

Such a treatment will be given in a later paper.*

Acknowledgements

The author would like to thank Professor Y. Nakamura for his advice and critical reading of the manuscript and Dr. Y. Muraoka for useful discussion. He is also much indebted to Mr. A. Takahashi for taking the data of thermal expansion of Fe.

References

1) M. Shiga: *Proc. Int. Conf. on Physics of Transition Metals*, Inst. Phys. Conf. Ser. No. 55, 1980, p. 241.
2) E. Callen and H. B. Callen: Phys. Rev. **139** (1965) A455.
3) M. Shiga and Y. Nakamura: J. Phys. Soc. Jpn. **26** (1969) 24.
4) O. K. Andersen, J. Madsen, U. K. Poulsen, O. Jepsen and J. Kollar: Physica **86-88B** (1977) 249.
5) V. Heine: Phys. Rev. **153** (1967) 673.
6) J. F. Janak and A. R. Williams: Phys. Rev. **B14** (1976) 4199.
7) M. Shiga: *Magnetism and Magnetic Materials* (N.Y., 1974) AIP Conf. Proc. No. 18, p. 463.

8) T. Moriya: J. Magn. & Magn. Mater. **14** (1979)1.
9) V. Korenman, J. L. Murray and R. E. Prange: Phys. Rev. **B16** (1977) 4032.
10) O. Gunnarsson: J. Phys. **F6** (1976) 587.
11) M. Shiga: Solid State Commun. **10** (1972) 1233.
12) J. Kanamori, Y. Teraoka and T. Jo: *Magnetism and Magnetic Materials* (N.Y., 1974) AIP. Conf. Proc. No. 24, p. 16.
13) S. Alexander and P. W. Anderson: Phys. Rev. **133** (1964) A1594.
14) T. Moriya: Prog. Theor. Phys. **33** (1965) 157.
15) C. P. Bean and D. S. Rodbell: Phys. Rev. **126** (1962) 104.
16) R. Minakata, M. Shiga and Y. Nakamura: J. Phys. Soc. Jpn. **41** (1976) 1435.
17) M. Shiga and Y. Nakamura: *Proc. Int. Conf. on Physics of Transition Metals*, Inst. Phys. Conf. Ser. No. 39, 1978, p. 540.
18) R. H. Donaldson: Phys. Rev. **157** (1967) 366.
19) S. Foner, A. J. Freeman, N. A. Blum, R. B. Franke1, E. J. McNiff, Jr. and H. C. Praddaude: Phys. Rev. **181** (1969) 863.
20) J. H. M. Stoelinga, R. Gersdorf and G. de Vries'. Physica **31** (1965) 349.
21) F. C. Nix and D. McNair: Phys. Rev. **60** (1941) 597.
22) R. Kohlhaas, Ph. Ddnner and N. Schmitz-pranghe: Z. Angew. Phys. **23** (1967) 245.
23) N. Ridley and H. Stuart: Br. J. App1. Phys. **1** (1968) 1291.
24) F. Richter and U. Lotter: Phys. Status Solidi **34** (1969) K149.
25) L. Patrick: Phys. Rev. **93** (1954) 384.
26) J. M. Leger, C; Loriers-Susse and B. Vodar: Phys. Rev. **B6** (1972) 4250.
27) H. Hasegawa: J. Phys. Soc. Jpn. **46** (1979) 1504.
28) J. Hubbard: Phys. Rev. **B20** (1979) 4584.
29) 29) L. Hodges, H. Ehrenreich and N. D. Lang: Phys. Rev. **152** (1966) 505.
30) 30) H. Tange and T. Tokunaga: I. Phys. Soc. Jpn. **27** (1969) 554.
31) J. Mathon: J. Phys. **F2** (1972) 159.
32) P. Weiss and R. Forrer: Ann. Phys. **5** (1926) 158.
33) O. Yamada and R. Pauthenet and J. C. Dicoche: J. Phys. **32** (France) (1971) C1-1119.
34) M. Matsumoto, T. Kaneko and H. Fujimori: J. Phys. Soc. Jpn. **26** (1969) 1083.
35) Y. Ishikawa, S. Onodera and K. J. Tajima: J. Magn. & Magn. Mater. **10** (1979) 183.
36) M. Hayase, M. Shiga and Y. Nakamura: J. Phys. Soc. Jpn. **34** (1973) 925.
37) M. F. Collins: Proc. Phys. Soc. **86** (1965) 973.
38) D. M. Edwards and E. P. Wohlfarth: Proc. R. Soc. London **303** (1968) 127.
39) E. P. Woh]farth: J. Phys. **C2** (1969) 68.
40) J. J. M. Franse: Physica **B+C86** (1977) 283.
41) T. Moriya and K. Usami: Solid State Commun. **34** (1980) 85.

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* *Note added in proof* - Recently, Hasegawa[1] and Kakehashi[2] have independently developed the theories of magnetovolume effects of metallic ferromagnets by using the functional integral method. Their results are consistent in many respects with our phenomenological theory as follows: 1) The volume change due to magnetism is mainly determined by the square of local magnetic moment. 2) The large ω_s of the Invar alloy may be attributable to the reduction of local moment with increasing temperature. 3) bcc-Fe should have rather small ω_s because of the stability of local moments even above the Curie temperature. However, the theoretical estimations of ω_s seems still too large compared with our experimental estimation.

1) H. Hasegawa: to be published in J. Phys. C.
2) Y. Kakehashi: private communication. A part of his work was published in J. Phys. Soc. Jpn. **49** (1980) 2421.