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The fixed-spin-moment method and fluctuations

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Abstract. Using the fixed-spin-moment method of Moruzzi and co-workers, we develop a general theory of the thermal and magneto-mechanical properties of weak itinerant ferromagnets in terms of spin and density fluctuations. Special attention is given to Invar effects.

1. Introduction

Spin fluctuation theory has added much to our present understanding of itinerant ferromagnetism [1]. In this paper we focus our attention on the weak limit of the general spin fluctuation theory, which was first dealt with in the frame of a Ginzburg–Landau theory of Murata and Doniach [2]. Later, Lonzarich was quite successful in applying this approach of the magnetic properties of weakly itinerant ferromagnets [3]. The magneto-mechanical properties, particularly the Invar effects, have been discussed less thoroughly [4]; for a recent review with special attention to the experiments we refer to Wassermann [5].

A crucial point of the theory is the connection of thermal properties with band structure calculations. Therefore the development of the fixed-spin-moment (FSM) method of Moruzzi *et al* [6], which gives the energy E as a function of the magnetisation M and the volume V, presents a firm basis for describing thermal effects of weak itinerant systems. Following essentially Murata and Doniach [2], we formulate a general fluctuation theory which includes spin fluctuations as well as density (volume) fluctuations. The latter ones are normally neglected; but FSM calculations have revealed that Invar effects might be traced back to a band structure, which exhibits two stationary points: a ferromagnetic minimum and a saddle point with vanishing moment, which differ only slightly in volume and energy [6]. In cases like this, it is not at all obvious that density fluctuations can be excluded, although the ferromagnetic phase transition is driven by magnetic fluctuations. Similar lines, discussing longitudinal spin fluctuations only have been followed by Entel *et al* [7].

A quite different approach, particularly to magneto-volume effect has been developed by Kim [8] and Zverev and Silin [9]. Their approach is based on the renormalisation of the frequency spectrum of phonons due to the ferromagnetism of the electrons. These theories take full account of quantum effects which should be important for low temperatures and which are left out of theories that treat thermal fluctuations as classical excitations. It is not quite clear whether quantum effects are relevant for the weak

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itinerant ferromagnet discussed in this paper. In a sense, both approaches are complementary; for higher temperatures, classical thermal fluctuations should dominate.

2. General theory

We assume that the energy of a metallic system with N atoms has been calculated at temperature $T = 0$ as function of the magnetisation per atom M_0 and the volume per atom V_0: $NE(M_0, V_0)$, where E is now the energy per atom. Thermal effects are described by adding magnetic fluctuations $\boldsymbol{m}(\boldsymbol{r})$ and volume (density) fluctuations $v(\boldsymbol{r})$ to M_0 and V_0, respectively, which depend on the spatial variable $\boldsymbol{r}$ only. $\boldsymbol{m}(\boldsymbol{r})$ and $v(\boldsymbol{r})$ are non-centred random variables. Changing to centred variables $\boldsymbol{m}(\boldsymbol{r}) \to \boldsymbol{m}(r) - \langle \boldsymbol{m}(r) \rangle$, where $\langle \boldsymbol{m}(\boldsymbol{r}) \rangle$ indicates a statistical mean value of the variable, we change from $\boldsymbol{M}_0 + \boldsymbol{m}(\boldsymbol{r})$ to $\boldsymbol{M}_0 + \langle \boldsymbol{m}(\boldsymbol{r}) \rangle + \boldsymbol{m}(\boldsymbol{r}) - \langle \boldsymbol{m}(r) \rangle$ and from $V_0 + v(r)$ to $V_0 + \langle v(r) \rangle + v(r) - \langle v(r) \rangle$. The quantities $\boldsymbol{M}_0 + \langle \boldsymbol{m}(r) \rangle$, $V_0 + \langle v(r) \rangle$ are now interpreted as thermodynamic variables, the magnetisation $\boldsymbol{M}$ and the volume V. $\boldsymbol{m}(r)$ and $v(r)$ are then random variables with vanishing mean values. The energy should be a complicated functional of $\boldsymbol{m}(r)$ and $v(r)$; however, we assume, as is usually done for weak itinerant ferromagnets, that the fluctuations vary on a spatial scale that is larger than the range of the interactions and use a local approximation for the functional. Non-local effects are taken into account by the lowest-order gradient terms. The Hamiltonian of the fluctuations is then given by

$$\mathcal{H} = \frac{1}{V} \int \mathrm{d}^3 r \left(E[\boldsymbol{M} + \boldsymbol{m}(r), V + v(r)] + \frac{C}{2} \sum_{ij} (\nabla_j m_i)^2 + \frac{D}{2} [\nabla v(r)]^2 \right) \tag{1}$$

where i, j denote components of the magnetic fluctuation and the gradient, respectively. In principle, one should introduce three constants C_i, $i = 1, 2, 3$, and three constants D_i as well, with $C_1 = C_2 = C_\perp$ and $C_3 = C_\parallel$, etc., because of a possible dependence of these constants on the magnetisation M. In the limit of weak itinerant ferromagnetism, however, one can neglect this dependence.

The free energy $F(M, V, T)$ is now given by $F = -k_B T \ln Z$ and the partition function Z by a classical integral over the phase space of the fluctuations Γ

$$Z = \int \mathrm{d}\Gamma \, \mathrm{e}^{-\beta \mathcal{H}} \qquad \beta = 1/k_B T. \tag{2}$$

The functional integration of the exponent can be performed only approximately. We approximate $\mathcal{H}$ by a general translationally invariant quadratic form $\mathcal{H}_0$:

$$\mathcal{H}_0 = \sum_i \frac{1}{V} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, \Omega_i(\boldsymbol{r} - \boldsymbol{r}') m_i(\boldsymbol{r}) m_i(\boldsymbol{r}') + \frac{1}{V} \int \mathrm{d}^3 r \int \mathrm{d}^3 r' \, \omega(\boldsymbol{r} - \boldsymbol{r}') v(\boldsymbol{r}) v(\boldsymbol{r}'). \tag{3}$$

The functions Ω_i and ω are chosen by the condition that the right-hand side of the Peierls inequality $F \leqslant F_0 + \langle H - H_0 \rangle_0$ is a minimum.

$$F_0 = -k_B T \ln Z_0 \qquad Z_0 = \int \mathrm{d}\Gamma \, \mathrm{e}^{-\beta \mathcal{H}_0}$$

where $\langle \, \rangle_0$ indicates a statistical mean value over the approximate Boltzmann distribution. We now introduce Fourier-transformed quantities

$$m_i(r) = \sum_k m_{ki}\, e^{ik\cdot r} \qquad v(r) = \sum_q v_q\, e^{iq\cdot r}$$

$$\Omega_i(r) = \frac{1}{NV}\sum_k \Omega_{ki}\, e^{ik\cdot r} \qquad \omega(r) = \frac{1}{NV}\sum_q \omega_q\, e^{iq\cdot r}$$

which gives

$$\mathcal{H}_0 = N \sum_{k,i} \Omega_{ki}|m_{ki}|^2 + N \sum_q \omega_q |v_q|^2.$$

Since $m_{ki} = m^*_{-ki}$ and $v_k = v^*_{-k}$, we have from $m_{ki} = x_{ki} + iy_{ki}$, $v_q = \rho_q + i\eta_q$,

$$x_{ki} = x_{-ki} \qquad y_{ki} = -y_{-ki} \qquad \rho_q = \rho_{-q} \qquad y_q = -y_{-q}.$$

The random variables are therefore not totally independent of each other. The space phase integral $\int d\Gamma$ is given as a product of integrals over the independepent variables $\{x_{ki}, y_{ki}, \rho_q, \eta_q\}$ with $k_z > 0, q_z > 0$.

The integrals are easily performed. Choosing the right-hand side of the Peierls inequality as the approximate free energy F one gets after integration:

$$\langle m_i^2(r)\rangle = \frac{k_B T}{2N}\sum_k \frac{1}{\Omega_{ki}} \qquad \langle v^2(r)\rangle = \frac{k_B T}{2N}\sum_q \frac{1}{\omega_q} \tag{4}$$

where we dropped the index in $\langle\ \rangle_0$. The approximate free energy is then:

$$F = NE(M, V) - \frac{k_B T}{2}\sum_{k,i} \ln\frac{\pi}{2N\beta\Omega_{ki}} - \frac{k_B T}{2}\sum_q \ln\frac{\pi}{2\beta\omega_q}$$
$$- \frac{k_B T}{2}\sum_{ki} 1 - \frac{k_B T}{2}\sum_q 1 + \frac{C}{2}\sum_{ki}\frac{k^2}{2\beta\Omega_{ki}} + \frac{D}{2}\sum_q \frac{q^2}{2\beta\omega_q} + N\varphi$$

where φ is the mean value

$$\varphi = \frac{1}{NV}\int d^3r\, \langle E(\boldsymbol{M} + \boldsymbol{m}, V + v) - E(M, V)\rangle. \tag{5}$$

Obviously φ is a function of the mean values of the local fluctuations $m_i^2(r)$, $v^2(r)$ and of M and V:

$$\varphi = \varphi(\{\langle m_i^2\rangle\}, \langle v^2\rangle, M, V).$$

$\{\Omega_{ki}\}$ and $\{\omega_q\}$ are now determined by $\partial F/\partial\Omega_{ki} = \partial F/\partial\omega_q = 0$ which gives

$$\Omega_{ki} = (C/2)k^2 + \partial\varphi/\partial\langle m_i^2\rangle \qquad \omega_q = (D/2)q^2 + \partial\varphi/\partial\langle v^2\rangle. \tag{6}$$

With the help of these equations the final form of the free energy is given by

$$F/N = E(M, V) - \frac{k_B T}{2N}\sum_{ki} \ln\frac{\pi}{2N\beta\Omega_{ki}} - \frac{k_B T}{2N}\sum_q \ln\frac{\pi}{2N\beta\omega_q}$$
$$+ \varphi - \sum_{i=1}^{3}\langle m_i^2\rangle\frac{\partial\varphi}{\partial\langle m_i^2\rangle} - \langle v^2\rangle\frac{\partial\varphi}{\partial\langle v^2\rangle}. \tag{7}$$

Equations (5)–(7) fully determine the thermal properties of the system.

3. The equations of state

The derivation of the equations of state from the free energy $F(T, M, V)$ depends on some assumptions concerning the dependence of the constants C and D on the magnetisation and volume. The dependence of C, which determines the excitation

energy of the spin fluctuations Ω_{ki}, has been discussed to some extent by Lonzarich [3]. In the weak limit, this dependence can be neglected to lowest order in M. The same kind of reasoning certainly applies to the dependence of D on M, which determines the energy of the density fluctuation, although the Kim–Silin approach is in essence based on this dependence; formally, this could be taken into account by a formal expansion of D in powers of M^2. Both dependences are left out here, the dependence on M as well as the dependence on V, the latter one because of the small change in volume (ca. 1%) over the whole temperature range.

Under these assumptions and using equations (4) and (6), it is easy to derive the magnetic equation of state from the free energy as given by equation (7):

$$H = (\partial F/\partial NM)_{T,V} = (\partial E/\partial M)_v + (\partial \varphi/\partial M)_{T,V,m_i,v} = (\partial \langle E\rangle/\partial M)_{T,V,m_i,v} \tag{8}$$

in short notation, where $\langle E\rangle$ is the generalised (including fluctuations) mean value of the energy of the FSM method. The indices in equation (8) indicate that T, V, $\{\langle m_i^2\rangle\}$ and $\langle v^2\rangle$ have to be kept fixed while performing the derivatives.

In very much the same way one obtains the mechanical equation of state

$$P = -(\partial F/\partial NV)_{T,M} = -[(\partial E/\partial V)_{T,M} + (\partial \varphi/\partial V)_{T,M,m_i,v}] = -(\partial \langle E\rangle/\partial V)_{T,M,m_i,v}. \tag{9}$$

The entropy S turns out to be very similar in form to the entropy derived by Murata and Doniach [2]; one obtains

$$S = \frac{k_B}{2}\sum_{ki}\left(1 + \ln\frac{\pi}{2N\beta\Omega_{ki}}\right) + \frac{k_B}{2}\sum_{q}\left(1 + \ln\frac{\pi}{2N\beta\omega_q}\right)$$

and from this results the specific heat at constant magnetic field and constant pressure P:

$$C_{H,P}(T) = \frac{k_B}{2}\sum_{ki} 1 + \frac{k_B}{2}\sum_{q} 1 - N\sum_i \langle m_i^2\rangle\left(\frac{\partial^2\varphi}{\partial T\,\partial\langle m_i^2\rangle}\right)_{H,P} - N\langle v^2\rangle\left(\frac{\partial^2\varphi}{\partial T\,\partial\langle v^2\rangle}\right)_{H,P}. \tag{10}$$

The first terms correspond to the classical Dulong–Petit law, $\Sigma_{ki}1$ and $\Sigma_q 1$ being the number of spin and density fluctuations, respectively. It has been tacitly assumed that the cut-off wave vectors k_c, q_c, which have to be introduced in equation (4), do not depend on the temperature T. The derivatives with respect to the temperature are partial because H and P have to be kept fixed, but they are total because one has to take into account the indirect dependence of φ on T via M, $V\{\langle m_i^2\rangle\}$ and $\langle v^2\rangle$.

Equations (8), (9) and (10) form a complete set of equations if supplemented by the definition of φ (equation 5), and by the self-consistency equations of the local fluctuations given by (4). If the integrations over $\boldsymbol{k}$ and $\boldsymbol{q}$ are performed, one gets from (4):

$$\langle m_i^2(r)\rangle = \frac{k_B TVk_c}{2\pi^2 c} f\left(\frac{C}{2}\frac{k_c^2}{\partial\varphi/\partial\langle m_i^2\rangle}\right)^{1/2} \tag{11}$$

with $f(x) = 1 - (1/x)\tan^{-1}(x)$. An analogous formula holds for $\langle v^2\rangle$. Because of the symmetry of the system one has $\langle m_1^2\rangle = \langle m_2^2\rangle = \langle m_\perp^2\rangle$, $\langle m_3^2\rangle = \langle m_\parallel^2\rangle$ for fluctuations that are perpendicular or parallel to the magnetisation. The unknown constants C, D, k_c, q_c can in principle be derived from experiment [3, 10]; this problem as well as the possible temperature dependence of the cut-off has been discussed extensively by Lonzarich [3].

If we restrict to magnetic phase transitions, the onset of a ferromagnetic instability should be connected with a pole in the $\boldsymbol{k}$-dependent susceptibility $\chi^{-1}(\boldsymbol{k}) \simeq \Omega_{\boldsymbol{k}}$ at $\boldsymbol{k} = 0$ for $T \geqslant T_C$, where T_C is the Curie temperature. At $T = T_C$ we have

$$(\partial\varphi/\partial\langle m_i^2\rangle)_{T=T_C} = 0. \tag{12}$$

On the other hand, the critical temperature is derived from the vanishing of the linear term in the magnetisation of the equation of state (for $H = 0$), i.e. from

$$(\partial E/\partial M^2 + \partial\varphi/\partial M^2)_{T=T_C} = 0 \tag{13}$$

assuming that E as well as φ are dependent on M^2 only. For consistency, both equations (12) and (13) must be fulfilled. It will be shown that this necessary condition restricts appreciably the numerical methods that can be used to evaluate the complete set of equations (8)–(11).

4. Applications

Explicit calculations can only be done numerically. Only in the limit $T \to 0$ φ can be given as an expansion in powers of the fluctuations since $\langle m_i^2\rangle, \langle v^2\rangle \to 0$ in this limit. The calculation is straightforward; one finds up to order 0 ($\langle m_i^6\rangle, \langle v^6\rangle$):

$$\begin{aligned}\varphi(\{\langle m_i^2\rangle\}, \langle v^2\rangle, M, V) = {} & \tfrac{1}{2}\langle v^2\rangle \frac{\partial^2 E}{\partial V^2} + \tfrac{1}{8}\langle v^2\rangle^2 \frac{\partial^4 E}{\partial V^4} + \sum_i \langle m_i^2\rangle \frac{\partial E}{\partial M^2} \\ & + 2M^2\langle m_\parallel^2\rangle \frac{\partial^2 E}{\partial (M^2)^2} + \tfrac{1}{2}\langle v^2\rangle\Big(\sum_i \langle m_i^2\rangle\Big) \frac{\partial^3 E}{\partial M^2\, \partial V^2} + M^2\langle m_\parallel^2\rangle \langle v^2\rangle \\ & \times \frac{\partial^4 E}{\partial (M^2)^2\, \partial V^2} + \tfrac{1}{2}\Big(3\sum_i \langle m_i^2\rangle^2 + \sum_{i\neq j} \langle m_i^2\rangle\langle m_j^2\rangle\Big) \frac{\partial^2 E}{\partial (M^2)^2} \\ & + 2M^2(3\langle m_\parallel^2\rangle^2 + 2\langle m_\parallel^2\rangle^2\langle m_\perp\rangle^2) \frac{\partial^3 E}{\partial (M^2)^3} + 2M^4\langle m_\parallel^2\rangle^2 \frac{\partial^4 E}{\partial (M^2)^4}.\end{aligned} \tag{14}$$

From this follow the equations of state. One finds in the lowest order of the fluctuations

$$\begin{aligned} H &= \frac{\partial E}{\partial M} + \tfrac{1}{2}\langle v^2\rangle \frac{\partial^3 E}{\partial M\, \partial V^2} + \frac{\langle m_\parallel^2\rangle}{2} \frac{\partial^3 E}{\partial M^3} + \frac{m_\perp^2}{M}\left(\frac{\partial^2 E}{\partial M^2} - \frac{1}{M}\frac{\partial E}{\partial M}\right) \\ -P &= \frac{\partial E}{\partial V} + \tfrac{1}{2}\langle v^2\rangle \frac{\partial^3 E}{\partial V^3} + \frac{\langle m_\perp^2\rangle}{M} \frac{\partial^2 E}{\partial M\, \partial V} + \frac{\langle m_\parallel^2\rangle}{2} \frac{\partial^3 E}{\partial V\, \partial M^2}. \end{aligned}$$

For $T \to 0$ the FSM energy $E(M, V)$ should be expanded in powers of $M - M_0$, $V - V_0$, where (M_0, V_0) denotes the minimum of energy for $T = 0$. Obviously $M - M_0$ and $V - V_0$ depend linearly on T as usual. For the change of the volume one gets:

$$\begin{aligned} V - V_0 = {} & \frac{1}{2}\frac{\langle v^2\rangle}{\Delta}\left(\frac{\partial^3 E_0}{\partial V_0^3}\frac{\partial^2 E_0}{\partial M_0^2} - \frac{\partial^3 E_0}{\partial M_0\, \partial V_0^2}\frac{\partial^2 E_0}{\partial M_0\, \partial V_0}\right) \\ & + \frac{\langle m_\parallel^2\rangle}{2\Delta}\left(\frac{\partial^3 E_0}{\partial V_0\, \partial M_0^2}\frac{\partial^2 E_0}{\partial M_0^2} - \frac{\partial^3 E_0}{\partial M_0^3}\frac{\partial^2 E_0}{\partial M_0\, \partial V_0}\right) \end{aligned}$$

with

$$\Delta = (\partial^2 E_0/\partial M_0\, \partial V_0)^2 - (\partial^2 E_0/\partial M_0^2)\partial^2 E_0/\partial V_0^2 < 0$$

since (M_0, V_0) is a minimum of the energy. In this approximation, the magneto-volume

effect depends only on the longitudinal spin fluctuations, and the coefficients depend only on the local properties of the minimum in the M, V plane.

There is a subtle point in using a power expansion in terms of the fluctuations. If this is used over the whole temperature range, then one can easily verify that the consistency equations (12) and (13) at $T = T_C$ can never be fulfilled by a finite series in powers of $\langle \boldsymbol{m}_i^2 \rangle$ and $\langle v^2 \rangle$, since equation (13) contains always additional higher-order derivatives in M^2 than equation (12). The only possibility of circumventing this problem is to use a polynomial for $E(\boldsymbol{M} + \boldsymbol{m}, V + v)$ that treats $\boldsymbol{M}$ and $\boldsymbol{m}$ on the same footing since it is easily shown that every term $\langle (\boldsymbol{M} + \boldsymbol{m})^{2\rho} \rangle$, where ρ is a positive integer, fulfills equations (12) and (13). Therefore it is not possible to use any other approximation scheme than polynominals in M and V to solve the equations of state numerically over the whole temperature range. This justifies the generalised Landau expansions of Shimizu [10] for instance, which should be interpreted as a mathematical approximation to the true function $E = E(M, V)$. For the simple case of a Landau expansion

$$E(M, V) = E(M) = (A/2)M^2 + (B/4)M^4$$

one then gets from equation (12)

$$\varphi(\{\langle m_i^2 \rangle\}, M) = \left(\frac{A}{2} + \frac{B}{2} M^2\right) \sum_i \langle m_i^2 \rangle + BM^2 \langle m_\parallel^2 \rangle + \frac{B}{4}\left(3 \sum_i \langle m_i^2 \rangle^2 + \sum_{i \neq j} \langle m_i^2 \rangle \langle m_j^2 \rangle\right)$$

from which one recovers the well known equation of state [3, 11]:

$$H = (A + 3\langle m_\parallel^2 \rangle + 2\langle m_\perp^2 \rangle)M + BM^3.$$

This case has been extensively discussed by various authors; near the critical temperature one has to face the possibility of a first-order phase transition, which is an artifact of the harmonic approximation as given by equation (3) [2, 3, 12]. Eventually, this difficulty may be overcome by improving the self-consistency equations (4) along the lines discussed by Lonzarich [3]†. As a result one obtains local moments $\langle m_i^2 \rangle$ which increase continuously with temperature (almost linearly) as one should expect from the underlying classical point of view.

Finally we want to discuss a simple example, suggested by D M Edwards, in order to show that spin fluctuations may contribute substantially to magneto-volume effects as observed in Invar alloys. For Fe_3Ni it was shown by Moruzzi *et al* [6] that in the (M, V) plane there is a minimum of the energy at $M_0 = 1.55$ Bohr magnetons/atom at a volume of $V_0 = 74$ au/atom. A saddle point is found with $M_1 = 0$ and $V_1 = 70$ au/atom, which differs in energy from the minimum by an amount $E_B = 6$ mRyd/atom. Due to the large magnetic moment Fe_3Ni cannot necessarily be interpreted as a weak itinerant ferromagnet; however, one might expect that on changing the composition—and thereby diminishing the magnetic moment—the overall band structure should not change very much.

An ansatz like

$$E = \lambda(V - \alpha M^2)^2 + \mu(V - V_0)^2$$

describes the overall band structure of this type of alloy, with

$$\alpha = \frac{V_0}{M_0^2} \qquad \lambda = \frac{E_B}{V_0 V_1} \qquad \mu = \frac{1}{V_0 - V_1} \frac{E_B}{V_0}.$$

The calculation is straightforward. For φ we get from equation (5) in this case:

† It is remarkable that the general FSM method does not necessarily lead to a first-order transition [13].

$$\varphi = (\lambda + \mu)\langle v^2\rangle + 4\alpha^2\lambda M^2\langle m_\parallel^2\rangle - 2\alpha\lambda(V - \alpha M^2)\sum_i \langle m_i^2\rangle + \lambda\alpha^2\left(3\sum_i \langle m_i^2\rangle^2 + \sum_{i\neq j}\langle m_i^2\rangle\langle m_j^2\rangle\right).$$

From this follow the equations of state:

$$H = -4\alpha\lambda M(V - \alpha M^2) + 4\alpha^2\lambda M(3\langle m_\parallel^2\rangle + 2\langle m_\perp^2\rangle)$$
$$-P = 2\lambda(V - \alpha M^2) + 2\mu(V - V_0) - 2\alpha\lambda(\langle m_\parallel^2\rangle + 2\langle m_\perp^2\rangle).$$

Neglecting transverse spin fluctuations we get from the equations of state for $H = P = 0$:

$$M^2(T) = M_0^2(1 - \langle m^2(r)\rangle/\langle m^2(r)\rangle_C)$$

where $\langle m^2(r)\rangle_C$ is the local fluctuation at $T = T_C$ and where $\langle m^2(r)\rangle$ as a classical quantity should increase more or less linearly with temperature.

$$\omega \equiv \frac{V - V_0}{V_0} = -2\left(\frac{V_0}{V_1} - 1\right)\frac{\langle m(r)^2\rangle}{M_0^2} \qquad T < T_C$$

$$\omega = \frac{V - V_0}{V_0} = -\left(1 - \frac{V_1}{V_0}\right)\left(1 - \frac{\langle m^2(r)\rangle}{M_0^2}\right) \qquad T > T_C.$$

From this

$$(\mathrm{d}\omega/\mathrm{d}T)_{T_C-0}/(\mathrm{d}\omega/\partial T)_{T_C+0} = -2V_0/V_1$$

assuming the continuity of the derivatives of the fluctuations. Furthermore we have

$$\langle m^2(r)\rangle_C = [V_1/(V_1 + 2V_0)]M_0^2.$$

From this the magneto-volume effect at $T = T_C$ is given as

$$\omega_{T=T_C} = -2(V_0 - V_1)/(V_1 + 2V_0).$$

Inserting the data of Fe_3Ni we have $\omega_{T=T_C} \simeq 0.04$ which is even a bit too large [5]. Assuming $\langle m^2\rangle = \langle m^2\rangle_C(T/T_C(P = 0))$ for pressure $P \neq 0$ and assuming furthermore that $\langle m^2\rangle_C$ does not depend on the pressure, one obtains for the variation in the Curie temperature with pressure P

$$(\mathrm{d}T_C/\mathrm{d}P)|_{P=0} = -T_C(V_0 - V_1)/2E_B.$$

The dependence of M, ω and $T_C(P)$ on V_0, V_1 and E_B is quite plausible.

The inclusion of transverse spin fluctuations changes these results appreciably. In self-evident notation we have

$$M^2(T) = M_0^2(1 - \langle m_\parallel^2\rangle/\langle m^2\rangle_{T=T_C}) - 2(\langle m_\perp^2\rangle - \langle m_\parallel^2\rangle)$$
$$\langle m^2\rangle_{T=T_C} = [V_1/(3V_1 + 2V_0)]M_0^2$$
$$\omega = -2(V_0/V_1 - 1)\langle m_\parallel^2\rangle/M_0^2 \qquad T < T_C$$
$$\omega = -(1 - V_1/V_0)(1 - 3\langle m^2\rangle/M_0^2) \qquad T \geqslant T_C$$
$$(\omega)_{T=T_C} = -2(V_0 - V_1)/(2V_0 + 3V_1)$$

and again assuming continuity of the derivatives,

$$(\mathrm{d}\omega/\mathrm{d}T)_{T_C-0}/(\mathrm{d}\omega/\mathrm{d}T)_{T_C+0} = \tfrac{2}{3}V_0/V_1.$$

The shift in the Curie temperature, $\mathrm{d}T_c/\mathrm{d}P$, is smaller by a factor of $\frac{1}{3}$.

Using the same assumptions it is not difficult to relate the discontinuity of the specific heat at $T = T_C$ to the band structure parameters V_0, V_1, M_0 and E_B. But since the resulting expression is somewhat cumbersome, it is omitted here.

From these results it is obvious that spin fluctuations contribute substantially to the magneto-volume effect (Invar) and it is clear that transverse fluctuations cannot be neglected. However, it should be kept in mind that the simple model does not take into account the more refined details of an explicit fixed spin moment calculation. A numerical calculation for the Fe_3Ni system is given in [13].

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