Zero-point spin fluctuations and the magnetovolume effect in itinerant-electron magnetism

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Quantum dynamical effects of zero-point spin fluctuations (SF) are shown to give rise to the strong spin anharmonicity effects neglected in the conventional SF theory of weak itinerant-electron magnetism, which is based on the weak SF coupling constraint. A theory of weak itinerant magnets is presented generalizing the quantum Ginzburg-Landau (GL) approach to account for large zero-point SF and spin anharmonicity effects in a wide temperature range both below and far above the Curie temperature. The theory is based on a variational procedure for the free energy treated as a functional of the magnetic susceptibilities which are defined self-consistently via the free energy. The magnetic equation of state and magnetovolume effect are analyzed in terms of thermal and zero-point SF. The theory presents the microscopic grounds for the phenomenological GL approach where the zero-point SF effects are incorporated in the model parameters and establishes a new link between the SF theory and the first-principles band-structure calculations.

I. INTRODUCTION

Presently, the spin-fluctuation (SF) theory of itinerant-electron magnetism successfully accounts for a large variety of thermal and kinetic properties of weakly ferromagnetic metals and is believed to be well established on the microscopic basis.[1] Initially introduced in terms of the fluctuating classical field variables[2] it was then related to the overdamped paramagnons within the Hubbard model[3] and Fermi-liquid concept[4] and incorporated quantum dynamical effects. Later the SF theory was equivalently reformulated in terms of the quantum Ginzburg-Landau (GL) approach directly focusing on the fluctuations of the magnetic order parameters and accounting for the SF dynamics as well.[5] The parameters of the GL model were treated on the phenomenological footing, which yields a good quantitative description of a series of weak itinerant magnets[1,5] and were also related to the first-principles band-structure calculations within, e.g., the fixed-spin-moment approach.[6–8]

However, up to now the approximations of the SF theory within both the microscopic and phenomenological GL approaches remain unclear. It should be emphasized that the conventional SF theory accounts only for thermally excited fluctuations which are assumed to be weakly coupled and described within the Gaussian or random-phase approximations. The quantum effects of zero-point SF were taken out of consideration, which is the crucial point of the SF theory. It has become commonplace to say that they give rise to the temperature-independent effects which may be included in the effective model parameters, e.g., in the exchange interaction constant.[1–5] However, that is not the case. Recent neutron-scattering experiments in weak itinerant-electron magnets[9–11] gave the direct evidence for the large zero-point SF amplitudes which essentially depend on temperature. As was pointed out by Takahashi[12] the temperature-dependent zero-point SF amplitudes may influence thermal properties of itinerant magnets. To account for this effect he assumed that the total SF amplitude including thermal and zero-point contributions is conserved. As we show below this constraint is not born out of thermodynamics for weak itinerant magnets and has a limited range of applicability related to the magnets with nearly localized atomic moments.

In this paper we present a different approach to analyze the zero-point SF effects in weak itinerant magnets based on a self-consistent thermodynamical treatment. Recently we have estimated the zero-point SF effects in some weak itinerant magnets[13] and shown them to give rise to the strong spin anharmonicity which *cannot* be treated within the conventional SF theory based on the weak-coupling constraint. To work out thermodynamics beyond the weak-coupling approximation instead of starting with the description of the Fermi quasiparticle states basing on the many-electron Hamiltonian or Fermi-liquid concept,[14] we use an equivalent but much more transparent quantum GL approach concentrating directly on the collective SF variables. We treat the free energy as a nonlinear functional of the magnetic susceptibilities and define it via the variational procedure. This yields a set of nonlinear differential equations which are solved in a relatively wide temperature range to obtain the magnetic equation of state and magnetovolume effect for strongly anharmonic itinerant magnets with account of the zero-point SF effects.

Her we would like to emphasize the difference between the quantum dynamical effects of the zero-point SF discussed below and the static electron correlation effects in narrow band systems (see, e.g., the review[15] and references therein) though the same term "quantum fluctuations" is sometimes used to describe both of them. The

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former effects arise due to the time correlations of collective dynamical variables[16] related to overdamped SF, paramagnons, and as we show below may essentially contribute to the thermal properties of itinerant magnets. The latter effects result from the static spatial correlations of individual electron variables[16] and are almost temperature independent, which can be incorporated into the effective parameters of a Fermi liquid[4,14,15] or of the adopted here GL model.[5]

II. SPIN ANHARMONICITY IN THE QUANTUM GINZBURG-LANDAU APPROACH

Focusing on the effects of collective spin excitations we begin with the conventional GL effective Hamiltonian for an isotropic weak itinerant ferromagnet (cf. Ref. 16):

$$\hat{H}_{\rm eff}=\frac{1}{2}\sum_{\mathbf{k}}\chi_0^{-1}(\mathbf{k})|\mathbf{M}(\mathbf{k})|^2 +\frac{1}{4}\gamma_0\sum_{\mathbf{k}_1+\mathbf{k}_2+\mathbf{k}_3+\mathbf{k}_4=0}[\mathbf{M}(\mathbf{k}_1)\cdot\mathbf{M}(\mathbf{k}_2)] \times[\mathbf{M}(\mathbf{k}_3)\cdot\mathbf{M}(\mathbf{k}_4)]\ , \quad (1)$$

where $\mathbf{M}(\mathbf{k})=\mathbf{M}\delta_{\mathbf{k},0}+\mathbf{m}(\mathbf{k})$ is the magnetic order parameter, $\mathbf{M}$ is the magnetization density, $\mathbf{m}(\mathbf{k})$ accounts for SF. Here γ_0 and $\chi_0(\mathbf{k})$ are the mode-coupling constant and the static inhomogeneous susceptibility in the absence of coupling. Below we assume that they incorporate static electron correlation effects and may be inferred from the band-structure calculations.[7,8] To complete our description of the dynamical SF effects we use the time-dependent GL equations[17,18]

$$\frac{1}{\Gamma(\mathbf{k})}\frac{\partial\mathbf{M}(\mathbf{k})}{\partial t}=-\frac{\delta\hat{H}_{\rm eff}}{\delta\mathbf{M}(-\mathbf{k})}\ , \quad (2)$$

with the relaxation rate $\Gamma(\mathbf{k})$ dominated by the Landau damping of SF.[1,3–5] Equations (1) and (2) fully determine the quantum GL model for itinerant-electron magnets (cf. Ref. 5). The Hamiltonian (1) accounts only for the lowest order mode-mode interactions and neglects the time and spatial dispersions of the coupling constant.[5,16,17] These approximations hold for weak itinerant magnets close to a ferromagnetic instability where the magnetic order parameter is relatively small providing expansions in powers of $\mathbf{M}(\mathbf{k})$, and long-wavelength low-frequency SF are known to play a predominant role.[1–5]

In the thermodynamical treatment of the conventional SF theory the effects of the SF coupling are described in the lowest order approximation in the SF amplitudes, actually in the Gaussian or random-phase approximations using the Peierls-Bogolyubov inequality for the free energy,

$$F\le F(\hat{H}_0)+\langle\hat{H}_{\rm eff}-\hat{H}_0\rangle\ . \quad (3)$$

Here $F(\hat{H}_0)$ is the free energy calculated with the noninteracting SF Hamiltonian

$$\hat{H}_0=\frac{1}{2\chi_0}M^2+\frac{\gamma_0}{4}M^4+\frac{1}{2}\sum_{\nu=t,l}\sum_{\mathbf{k}}\chi_\nu^{-1}(\mathbf{k})|m_\nu(\mathbf{k})|^2\ , \quad (4)$$

where $\chi_0=\chi_0(0)$, $\chi_\nu(\mathbf{k})$ are the transverse ($\nu=t$) and longitudinal ($\nu=l$) inhomogeneous magnetic susceptibilities found either from the thermodynamical relations[1,3,5] or from the minimization procedure,[2,6] and $\langle\cdots\rangle$ indicates the statistical average related to $\hat{H}_0$. The approximation of the conventional SF treatment[1–6] is to drop the SF coupling term $\langle\hat{H}_{\rm eff}-H_0\rangle$ in Eq. (3) while describing thermal properties of itinerant magnets. As we have pointed out recently[13] this approach is valid only in the weak-coupling limit when the spin anharmonicity parameter

$$g_\nu=2\gamma_0\sum_{\omega,\mathbf{k}}{\rm Re}\chi_\nu(\omega,\mathbf{k})\delta m_\nu^2(\omega,\mathbf{k})\sim\left|\frac{\partial(\delta m_\nu^2)}{\partial(M^2)}\right| \quad (5)$$

is small. The parameter (5) also describes the dynamical anharmonic effects[18] defined by the nonlinear equations of motion (2). Here

$$\delta m_\nu^2=\sum_{\omega,\mathbf{k}}\delta m_\nu^2(\omega,\mathbf{k})=(\delta m_\nu^2)_T+(\delta m_\nu^2)_{\rm zp} \quad (6)$$

are the averaged amplitudes of SF including the thermal

$$(\delta m_\nu^2)_T=4\hbar\sum_{\omega,\mathbf{k}}N_\omega{\rm Im}\chi_\nu(\omega,\mathbf{k}) \quad (7)$$

and zero-point

$$(\delta m_\nu^2)_{\rm zp}=2\hbar\sum_{\omega,\mathbf{k}}{\rm Im}\chi_\nu(\omega,\mathbf{k}) \quad (8)$$

contributions, $\delta m_\nu^2(\omega,\mathbf{k})$ is the spectral density of SF, $N_\omega=[\exp(\hbar\omega/k_BT)-1]^{-1}$,

$$\sum_{\omega,\mathbf{k}}=\sum_{\mathbf{k}}\int_0^\infty\frac{d\omega}{2\pi}$$

and

$$\chi_\nu^{-1}(\omega,\mathbf{k})=\chi_\nu^{-1}(\mathbf{k})-i\frac{\omega}{\Gamma(\mathbf{k})}=\chi_\nu^{-1}+c\mathbf{k}^2-i\frac{\omega}{\Gamma k} \quad (9)$$

are the inverse dynamical susceptibilities following from the equations of motion (2). Here we assume the static susceptibilities $\chi_\nu(\mathbf{k})=(\chi_\nu^{-1}+c\mathbf{k}^2)^{-1}$ and relaxation rate $\Gamma(\mathbf{k})=\Gamma k$ to have the conventional form[1–5] provided the frequency $\omega\le\omega_c$ and wave vector $k\le k_c$ are in the paramagnon region. Here the constants c and Γ describe the spatial dispersion and relaxation rate, $\omega_c\approx kv_F$ and k_c are the cutoff frequency and wave vector defined by the Stoner continuum boundary and Fermi momentum, respectively, and v_F is the Fermi velocity. The form (9) for the dynamical susceptibility is supported by the inelastic neutron-scattering experiments in weak itinerant magnets[19] and was shown to hold over the whole Brillouin zone for a wide frequency range $0<\omega<7.9\cdot k_BT_c/\hbar$ (Ref. 10) where T_c is the Curie temperature.

Not far from the Curie temperature, when the inverse magnetic susceptibilities are small enough,

$$\chi_{t,l}^{-1}\ll ck_T^2\ , \quad (10)$$

one may expand thermal SF amplitudes (7) in powers of $\chi_{t,l}^{-1}$:

$$(\delta m_v^2)_T = \delta m_T^2 - \frac{k_B T}{4\pi c}(c\chi_v)^{-1/2} + \cdots \ . \qquad (11)$$

Here k_T is the characteristic wave vector of thermal SF given by $k_T = k_c$ in the classical high-temperature limit, $T \gg T_m$, and $k_T = (T/T_m)^{1/3} k_c$ in the low-temperature quantum regime $T \ll T_m$, where $k_B T_m \sim \hbar\Gamma c k_c^3$ is the maximum energy of SF, and

$$\delta m_T^2 = \frac{k_B T k_T}{2\pi^2 c} \qquad (12)$$

is the squared amplitude of thermal SF at $\chi_v^{-1} = 0$ (see, e.g., Ref. 5). With Eq. (11) one easily estimates the thermal contribution

$$\sim \sqrt{\tau_G T_c / |T - T_c|}$$

to the anharmonicity parameter (5), where[16,17]

$$\tau_G = \frac{1}{32\pi^2}\left[\frac{k_B}{\Delta C \xi_0^3}\right]^2 \qquad (13)$$

is the Ginzburg parameter expressed in terms of the specific-heat jump at T_c, $\Delta C = \alpha^2 / 2\gamma T_c$, and the magnetic correlation length $\xi_0 = \sqrt{c/\alpha}$, where $\alpha = \partial(\chi^{-1})/\partial \ln T$. Here χ^{-1} and γ are the coefficients in the Landau free energy (see Sec. III). The constraint of weak coupling of thermal SF thus lead to the well-known Ginzburg-Levanyuk criterion

$$\left|\frac{T - T_c}{T_c}\right| \gg \tau_G \qquad (14)$$

previously obtained for itinerant magnets by other means.[2,4] The violation of this inequality leads to the breakdown of the SF theory in the critical region due to the crucial increase of the effects of thermal SF anharmonicity (cf. Ref. 17).

Similarly expanding the squared zero-point SF amplitudes (8), provided

$$\chi_{t,l}^{-1} \ll c k_c^2 \ , \qquad (15)$$

we have

$$(\delta m_v^2)_{zp} = \delta m_c^2 - g_0 (\gamma_0 \chi_v)^{-1} + \cdots \ , \qquad (16)$$

where

$$\delta m_c^2 = \frac{\hbar \Gamma k_c^4}{16\pi^3}[\ln(1+f^2) + f^2 \ln(1+f^{-2})] \qquad (17)$$

is the squared amplitude of zero-point SF with $\chi_v^{-1} = 0$, $f = v_F / \Gamma c k_c^2$, and

$$g_0 = \frac{\Gamma \gamma_0 k_c^2}{4\pi^3 c} f \tan^{-1}\left[\frac{1}{f}\right] \sim \frac{\gamma_0 \delta m_c^2}{c k_c^2} \qquad (18)$$

defines the zero-point SF contribution to the anharmonicity parameter (5). The constraint of weak coupling imposes a rather strong restriction on the anharmonicity of zero-point SF,

$$g_0 \ll 1 \ , \qquad (19)$$

which together with the Ginzburg-Levanyuk criterion (14) limits the validity of the conventional SF theory.

It should be mentioned that in the weak spin anharmonicity limit (19) the temperature dependence of the zero-point SF amplitudes (16) arising from the variation of χ_v is negligibly small. Thus we may conclude that the conventional SF theory[1-5] neglecting the variation of the zero-point SF amplitudes is well established in the limit of weak spin anharmonicity.

However, according to our recent estimates[13] (see Table I) based on the neutron-scattering experiments the spin anharmonicity parameter (18) in weak itinerant magnets is not small and the conventional SF approach[1-5] based on the constraint of the weak coupling is not applicable for them.

III. FREE ENERGY AND MAGNETIC EQUATION OF STATE

To describe the large spin anharmonicity effects due to zero-point SF one has to work out thermodynamics of itinerant magnets beyond the weak-coupling approximation taking into account the effects of the variation of the zero-point SF amplitudes. This may be done within the standard perturbation theory (see, e.g., Refs. 17 and 20 basing either on the GL or many-electron Hamiltonians. Here we would like to mention a recent work of Steiner, Albers, and Sham[21] who took into account the effects of zero-point SF within the local-spin-density calculation of the band structure of transition metals up to the second order in SF amplitudes. However, in systems with strong spin anharmonicity, and we believe weak itinerant magnets fall into this category, it is hardly possible to use a finite-order perturbation theory.

In this paper we present a different approach based on a self-consistent variational procedure to calculate the free energy of a strongly anharmonic itinerant magnet. Below we use the following constraints. First, we describe the finite temperature properties of a magnet within the GL model at a fixed magnetization M, volume V, and SF spectrum defined by dynamical susceptibilities $\chi_v(\omega, \mathbf{k})$. Second, instead of a direct calculation of $\chi_v(\omega, \mathbf{k})$ from the nonlinear time-dependent GL equations (2) we assume for them the conventional form (9) with c and Γ independent on M, V, and T. Third, we neglect the effects of coupling of SF to the displacive fluctuations of the crystal lattice though this may be important for structurally unstable magnets.[22] Thus, we treat the free-energy density

TABLE I. Zero-point SF effects in weak itinerant magnets MnSi, Ni_3Al, and $ZrZn_2$. Magnetic moments M_0 and $(M_L)_{tot}$ for $T = 0$ are given in μ_B per magnetic atom. The values for g, γ, M_0, and $(M_L)_{tot}$ are taken from Ref. 13.

	g	g_0	ξ	γ (G^{-2})	γ_0 (G^{-2})	M_0	$(M_L)_{tot}$
MnSi	0.18	5.4	0.1	0.15	4.9×10^{-3}	0.4	0.85
Ni_3Al	0.15	1.1	0.25	0.53	7.0×10^{-2}	0.075	0.46
$ZrZn_2$	0.10	0.32	0.5	2.0	0.63	0.157	0.72

$$F=F(M,V,T,\chi_t,\chi_l) \tag{20}$$

as a functional of M, V, T, and static homogeneous susceptibilities defined by the thermodynamic relations

$$\chi_t=\frac{M}{B},\quad \chi_l=\left[\frac{\partial M}{\partial B}\right]_V . \tag{21}$$

Finally, we use the equations of state

$$B=\left[\frac{\partial F}{\partial M}\right]_{V,\chi_\nu}+\sum_{\nu=t,l}\left[\frac{\partial F}{\partial(\chi_\nu^{-1})}\right]_V\left[\frac{\partial(\chi_\nu^{-1})}{\partial M}\right]_V , \tag{22}$$

$$P=-\left[\frac{\partial(FV)}{\partial V}\right]_{MV,\chi_\nu} -\sum_{\nu=t,l}\left[\frac{\partial F}{\partial(\chi_\nu^{-1})}\right]_{MV}\left[\frac{\partial(\chi_\nu^{-1})}{\partial \ln V}\right]_{MV} \tag{23}$$

following from the conventional minimization of the thermodynamic potential $(F+P-MB)V$, where B and P are the magnetic field and pressure, respectively. Equations (20)–(23) form a set of differential equations defining the finite-temperature free energy of a dynamical magnetic system.

To solve Eqs. (20)–(23) one has to know the form of the functional (20) which may be rather complicated, particularly, at low temperatures. However, the problem may be treated easily not far from the Curie temperature by expanding the free energy in powers of the inverse susceptibilities similar to (11) and (16), provided $\chi_{t,l}^{-1}$ are small enough and satisfy inequalities (10) and (15). Below we assume (15) to hold for weak itinerant magnets down to the zero temperature, which allow us to consider their ground-state properties.

With the equality

$$\frac{\partial F}{\partial(\chi_0^{-1})}=\frac{1}{2}\left[M^2+\sum_{\nu=t,l}\delta m_\nu^2\right] \tag{24}$$

following from the Hamiltonian (1) the expansion may be written in the form

$$F=F_0+\frac{1}{2\chi_0}M^2+\frac{\gamma_0}{4}M^4 +\frac{1}{2}\sum_{\nu=t,l}\frac{1}{\zeta_\nu}\left\{[\delta m_c^2+\delta m_T^2]\chi_\nu^{-1}-\frac{k_BT}{6\pi c^{3/2}}\chi_\nu^{-3/2} -\frac{g_0}{2\gamma_0}\chi_\nu^{-2}+\cdots\right\} . \tag{25}$$

Here F_0 denotes the contribution independent on the magnetization, the terms with M^2 and M^4 are related to the Hartree-Fock approximation of the Stoner model, the last term in the right-hand side of Eq. (25) describes the SF contribution, and

$$\zeta_\nu=\frac{\partial(\chi_\nu^{-1})}{\partial(\chi_0^{-1})} . \tag{26}$$

According to (16) the contribution containing $g_0\chi_\nu^{-2}$ accounts for the variation of the zero-point SF amplitudes, and the terms with $\chi_{t,l}^{-3/2}$ define the conventional GL fluctuation free energy giving rise to the divergent second thermodynamical derivatives near T_c. Below we neglect the effects of the latter, which are small aside the critical region when the Ginzburg-Levanyuk criterion (14) is satisfied.

The coefficients ζ_ν in (25) are affected by spin anharmonicity and in the Gaussian or random-phase approximations of the SF theory[1–5] are equal to 1. The same constraint, $\zeta_\nu=1$, was used in Ref. 13 to discuss the effects of the variation of the zero-point SF amplitudes due to spin anharmonicity. Here we account for the anharmonic effects beyond these approximations assuming that ζ_ν are the functions of the spin anharmonicity parameter g_0 only and are independent on the susceptibilities. Below we will verify this assumption and find (26) via the variational procedure.

Using the functional (25) we may write the solution of the differential equations (20)–(23) in the form of the Landau free energy

$$F=F_0+\frac{3}{2\zeta\chi(T)}\left[\delta m_c^2+\delta m_T^2-\frac{g}{2\gamma\chi(T)}\right] +\frac{1}{2\chi(T)}M^2+\frac{\gamma}{4}M^4 , \tag{27}$$

where the coefficients $\chi^{-1}(T)$ and γ are given by

$$\chi^{-1}(T)=\zeta\chi_0^{-1}+5\gamma(\delta m_c^2+\delta m_T^2) , \tag{28}$$

$$\gamma=\gamma_0\frac{1-5g}{1+6g} . \tag{29}$$

Here g is the renormalized spin anharmonicity parameter defined by

$$g_0=g\frac{1+fg}{1-5g} . \tag{30}$$

We also obtain the constants

$$\zeta_t=\zeta_l=1-5g=\zeta , \tag{31}$$

which are independent on the magnetic susceptibilities, verifying the approximation we used above.

We emphasize that the free energy (27) is valid in a wide temperature range (see Sec. V) and holds also in the low-temperature limit when the effects of thermal SF are negligible and the inverse susceptibilities (15) are small enough to allow the expansion (25).

In the limit $\delta m_c^2, g_0=0$ when the zero-point SF effects are neglected Eqs. (27)–(31) yield the Landau free energy corresponding to the conventional SF theory.[1–6] Zero-point SF essentially affect the ground state of an itinerant magnet and renormalize the GL coefficients χ_0^{-1} and γ_0. The Stoner criterion

$$\zeta\chi_0^{-1}+5\gamma\delta m_c^2<0 \tag{32}$$

is also modified regarding the Hartree-Fock criterion, $\chi_0^{-1}<1$. The zero-point effects tend to suppress a ferromagnetic instability by adding a contribution $\sim\delta m_c^2$ and reducing the negative term $\sim\chi_0^{-1}$. According to (1) the contribution to (32) containing δm_c^2 comes from the coupling of zero-point SF to the order parameter and is positive, provided $\gamma_0>0$. The factor $\zeta<1$ in the term with χ_0^{-1} accounts for the effects of spin anharmonicity beyond the weak-coupling approximation of the existing theory.[1–5] It is worth noting that, similarly to the dynamical effects of zero-point SF discussed here, a tendency to ferromagnetism may be also suppressed by the static electron correlations.[15]

The effects of spin anharmonicity due to zero-point SF also reduce the SF coupling constant γ which according to Eqs. (29) and (30) is approximately given by

$$\gamma=\begin{cases}\gamma_0(1-11g_0), & g_0\ll 1;\\ \gamma_0/5g_0, & g_0\gg 1\end{cases} \tag{33}$$

and vanishes in the limit of strongly anharmonic magnets. Similarly, from Eqs. (30) and (31) it follows approximately

$$g=\begin{cases}g_0(1-11g_0), & g_0\ll 1;\\ 1/5, & g_0\gg 1,\end{cases} \tag{34}$$

$$\zeta=\begin{cases}1-5g_0, & g_0\ll 1;\\ 11/25g_0, & g_0\gg 1.\end{cases} \tag{35}$$

According to Eq. (35) in the strong spin anharmonicity limit $g_0\gg 1$ the coefficient ζ vanishes resulting in the increase of the SF contribution to the free energy (25) with respect to the weakly-coupling, Gaussian or random-phase approximations.

Substituting the free energy (27) into the magnetic equation of state (22) we obtain it in the following explicit form:

$$\frac{B}{M}=\chi^{-1}(0)+\gamma(M^2+5\delta m_T^2)\ , \tag{36}$$

which accounts for both thermal and zero-point SF effects. We emphasize that it has essentially the same form as that arising in the conventional SF theory with zero-point SF neglected.[4–6,22,23] The effects of the latter are incorporated in the renormalized GL coefficients $\chi^{-1}(0)$ and γ which essentially differ from the initial ones, χ_0^{-1} and γ_0. Assuming that the latter are known from band-structure calculations[7,8] we point out that formulas (28)–(31) present the microscopic grounds for the quantum GL approach for itinerant magnetism relating it to the first-principles band theory. Taking into account that the calculated coefficients $\chi^{-1}(0)$ and γ in the free energy (27) and in the magnetic equation of state (36) are reduced due to the zero-point SF effects, compared to the unrenormalized values, χ_0^{-1} and γ_0, we may also conclude that the conventional SF theory[1–5] overestimates SF effects.

IV. MAGNETOVOLUME EFFECT

Now we discuss the magnetovolume effect where zero-point SF manifest themselves most directly. The well-known result for the magnetic contribution to the volume strain of the phenomenological Moriya-Usami theory based on the GL approach reads as[24]

$$\omega_m=\frac{C_0}{K}(M_L^2)_T\ , \tag{37}$$

where $C_0=(1/2)V^2\partial(\chi_0V)^{-1}/\partial V$ is the magnetoelastic coupling constant defined by the initial GL parameter χ_0, K is the bulk modulus, and

$$(M_L^2)_T=M^2\sum_\nu(\delta m_\nu^2)_T\simeq M^2+3\delta m_T^2 \tag{38}$$

is the averaged squared local magnetic moment incorporating the effects of thermal SF. Later (37) was justified by the microscopic treatment[22,23] accounting for the effects of charge-density fluctuations, long-range Coulomb interactions and magnetodeformational coupling, and was generalized to apply for the fixed-spin-moment band-structure calculations.[6]

One would expect that zero-point SF give an additional temperature dependence of the magnetovolume effect compared to (37). To account for the influence of zero-point SF we use the free energy given by Eqs. (25) and (27) to calculate the equation of state (23) in the following explicit form:

$$P=P_0(V,T)+C_0(M_L^2)_{\rm tot}\ , \tag{39}$$

where $P_0=-\partial(F_0V)/\partial V$ is the nonmagnetic contribution and

$$(M_L^2)_{\rm tot}=(M_L^2)_T+\sum_\nu(\delta m_\nu^2)_{\rm zp}$$

is the total squared local magnetic moment which incorporates effects of both thermal and zero-point SF. Here we assumed that weak itinerant magnets are sufficiently close to a magnetic instability, and the volume dependence of their free energy comes mainly from $\chi_0=\chi_0(V)$, provided

$$\left|\frac{\partial\ln\chi_0}{\partial\ln V}\right|,\quad \left|\frac{\partial\ln\chi(0)}{\partial\ln V}\right|\gg 1\ .$$

This allows us to neglect in the equation of state (39) a term related to the specific heat[25] and small contributions resulting from the relatively weak volume dependencies of the parameters c, Γ, γ_0, k_c, and v_F. We mention that formula (39) can be also obtained straightforwardly from the Hamiltonian (1) by averaging the derivative $-\partial(\hat{H}_{\rm eff}V)/\partial V$, and has a wider range of validity than the present derivation based on the expansion of the free energy (25) would suggest.

Using the magnetic equation of state (36) and the expansion (16) for the zero-point SF amplitudes we can present the total squared magnetic moment in the form

$$(M_L^2)_{\rm tot}=\zeta(M_L^2)_T+3\left[\delta m_c^2-\frac{g}{\chi(0)\gamma}\right]\ . \tag{40}$$

Equations (39) and (40) yield the following explicit expression for the magnetovolume effect:

$$\omega_m=\frac{C_0}{K}(M_L^2)_{\rm tot}=\frac{C}{K}(M_L^2)_T+3\frac{C_0}{K}\left[\delta m_c^2-\frac{g}{\chi(0)\gamma}\right]\ , \tag{41}$$

accounting for both thermal and zero-point SF. Here $C=-(1/2)V^2\partial(\chi V)^{-1}/\partial V$ is the renormalized magnetoelastic coupling constant which may be related to C_0, $C\simeq\zeta C_0$.

It follows from (41) that the magnetovolume effect in weak itinerant magnets is proportional to the total squared local magnetic moment $(M_L^2)_{\text{tot}}$ incorporating thermal and zero-point SF effects. According to Eq. (25) in the Hartree-Fock approximation when SF effects are neglected, formulas (40) and (41) reduce to $(M_L^2)_{\text{total}}=M_L^2$ end to the familiar expression for the magnetovolume effect in the Stoner model, $\omega_m\sim M^2$ (see Ref. 1). Equations (40) and (41) generalize the results (37) and (38) of the conventional SF theory with account of zero-point SF effects. According to Eqs. (40) and (41) zero-point SF may affect the temperature dependencies of $(M_L^2)_{\text{tot}}$ and ω_m reducing it by a factor $\zeta^{-1}=(1-5g)^{-1}>1$—apart from the temperature-independent contributions containing δm_c^2 and $\chi^{-1}(0)$. This reduction of the magnetovolume effect by zero-point SF may be incorporated into the renormalized magnetoelastic coupling constant C.

In the weak spin anharmonicity limit when $g_0\ll 1$, formulas (40) and (41) reduce to Eqs. (37) and (38) of the Moriya-Usami theory[24] after neglecting temperature independent contributions. In the strong-coupling limit when $g_0\gg 1$ and, according to (35), $\zeta\ll 1$, it follows from (40) that the variation of the zero-point SF amplitude compensates the thermal SF contribution $(M_L^2)_T$ to the total squared moment which becomes temperature independent,

$$(M_L^2)_{\text{tot}}=\text{const.} \tag{42}$$

This limit is related to magnets with localized atomic spins fixed by the Hund's rule (see, e.g., Refs. 1, 12, and 15).

Recently the constraint (42) was used by Takahashi[12] to describe thermal properties of itinerant magnets with account of the zero-point SF effects. The magnetic equation of state in his microscopic model results without a thermodynamical description from combining Eqs. (16) and (42) and may be written in the form (36) with the coefficient $\gamma=\gamma_0/5g_0$ which follows from our formula (33) for $g_0\gg 1$. We may conclude that the description of the zero-point SF effects within the model of Ref. 12 is supported by our thermodynamical treatment only in the limit of strong spin anharmonicity and is related to the magnets with nearly localized atomic moments. It should be also mentioned that the description of the magnetovolume effect in this approach[12] requires the account of the spatial dispersion of the magnetoelastic coupling constant.[26] Otherwise, according to (41) ω_m turns out to be independent on temperature.

V. DISCUSSIONS AND CONCLUSIONS

In this work we analyzed the zero-point SF effects in anharmonic weak itinerant magnets basing on the expansion of the free energy in terms of the inverse magnetic susceptibilities, which is a central point of our theory. This allowed us to present the results in a simple form of the Landau theory of phase transitions. On the other hand, this imposes certain restrictions which we discuss below.

Above we have already commented that our approach is valid for weak itinerant magnets at low temperatures provided the inequality (15) holds down to $T=0$. At finite temperatures besides the Ginzburg-Levanyuk criterion (14) our approach is limited by the condition (10) allowing the expansion of the thermal SF contribution to the free energy (25). First we discuss the limit of low-T_c itinerant magnets,

$$T_c\ll T_m\ , \tag{43}$$

which is realized in the conventional weak ferromagnets MnSi, Ni_3Al, and $ZrZn_2$ (see Refs. 5 and 13). With account of Eqs. (12) and (36) and the estimate $\delta m_c^2\sim\hbar\Gamma k_c^4$ following from Eq. (17), one finds that condition (43) is satisfied for these systems if the spontaneous magnetization $M_0=M(T=0)$ is less than the zero-point SF amplitude,

$$M_0^2\ll\delta m_c^2\ . \tag{44}$$

Using Eq. (18) we may express inequalities (10) and (15) in the following explicit form:

$$\left|\left[\frac{T}{T_c}\right]^{4/3}-1\right|\ll\frac{1}{5g}\left[\frac{T_m}{T_c}\right]^{4/3},\quad\frac{1}{5g}\left[\frac{TT_m}{T_c^2}\right]^{2/3}. \tag{45}$$

For the low-T_c magnets this condition is satisfied not only near T_c when $|T-T_c|\ll T_c$, but also in a wide temperature range far above T_c, provided

$$T\ll(5g)^{-3/4}T_m\ . \tag{46}$$

Similarly we obtain that for high-T_c itinerant magnets, when

$$T_c\gg T_m\ , \tag{47}$$

the spontaneous magnetization must exceed the zero-point SF amplitude,

$$M_0^2\gg\delta m_c^2\ . \tag{48}$$

One may expect that in this high-temperature classical limit the zero-point SF effects are negligibly small. However, in the vicinity of T_c the cancellation of the terms with $\chi_0^{-1}M^2$ and $\delta m_T^2\chi_\nu^{-1}$ makes the zero-point SF contribution $-g\chi_\nu^{-2}$ to the free energy (25) important. Analogous to the condition (45) we rewrite the inequalities (10) and (15) for high-T_c magnets in the form

$$\left|\frac{T}{T_c}-1\right|-\frac{1}{5g}\frac{T_m}{T_c}\ll 1\ . \tag{49}$$

From the relations (47) and (49) it follows that for high-T_c magnets with strong spin anharmonicity effects $(5g\approx 1)$ our approach is valid only in the vicinity of T_c, contrary to the case of low T_c magnets.

It is possible to make quantitative estimates of the effects of zero-point SF and spin anharmonicity for weak itinerant-electron magnets, using the recent neutron-scattering investigations.[5,10,19] According to Eq. (18) one would expect strong spin anharmonicity effects caused by zero-point SF in magnets with weak spatial dispersion of the magnetic susceptibilities when the constant c in (9) is small.

Our estimates for weak itinerant magnets MnSi, Ni_3Al, and $ZrZn_2$ support this suggestion. In Table I we present the spin anharmonicity parameters[13] $g=(\gamma/\gamma_0)g_0$ and $\zeta=1-5g$ calculated from Eq. (18) with the parameters c, Γ, k_c, and γ inferred from the neutron-scattering and magnetic data.[5,10,19] The Fermi velocity defining the cutoff frequency $\omega_c=kv_F$ was estimated from the relation $v_F\approx(\pi/2)\Gamma\chi_p^{-1}$, exact for a parabolic energy band, where χ_p is the Pauli susceptibility taken from the band-structure calculations (see Ref. 13). From Eqs. (29) and (30) we estimate the unrenormalized quantities g_0 and γ_0 which are also presented in Table I. We may conclude that spin anharmonicity effects caused by zero-point SF play an important role in all these materials which is reflected in the large anharmonicity parameters g_0, varying from 0.32 for $ZrZn_2$ to 5.4 for MnSi, and in the strong renormalization of the coupling constant γ related to γ_0. The parameter ζ essentially deviates from the value $\zeta=1$ corresponding to the weak-coupling limit of the conventional SF theory. We mention that the anharmonic effects are most pronounced in MnSi where the spatial dispersion described by the coefficient c is the weakest among these materials.[5,10,19]

In Table I we also present the zero-temperature values for the local magnetic moment[13] $(M_L)_{\text{tot}}=\sqrt{(M_L^2)_{\text{tot}}}$ calculated similarly to g from Eqs. (17) and (40), which should be compared with the spontaneous magnetization M_0. We conclude that zero-point SF give a significant contribution to $(M_L)_{\text{tot}}$ which turns out to be 2 to 6 times larger than the spontaneous magnetization. Our estimate $(M_L)_{\text{tot}}=0.85\mu_B$ (where μ_B is the Bohr magneton) for MnSi may be compared with the polarized neutron-scattering data of Ziebeck *et al.*[9] They measured the inelastic-scattering cross section integrated over the instrument resolution -10 meV defining the energy cutoff. After integrating this over the inverse atomic volume they estimated the amplitude of SF in MnSi at 11 K, $0.84\mu_B$, which yields the total local magnetic moment $0.93\mu_B$. Assuming that thermal SF effects at this temperature are small[10] we see that the approach presented here gives a reasonable description of zero-point SF effects in weak itinerant magnets.

To conclude, the analysis presented above suggests the importance of the zero-point SF effects in itinerant magnets with strong spin anharmonicity. The role of zero-point SF is manyfold. First, they directly affect the zero-temperature properties of metals resulting, e.g., in the shift of the Stoner criterion. Second, due to their large amplitude zero-point SF lead to the strong spin anharmonicity which in turn gives rise to the essential temperature dependence of their amplitude caused by the coupling to thermal SF. Finally, effects of zero-point SF anharmonicity strongly influence the coupling of thermal SF and result in the breakdown of the conventional SF theory based on a constraint that the renormalization of this coupling is negligibly small. None of these aspects have received a satisfactory treatment.

In this paper we presented the description of the zero-point SF effects in strongly anharmonic itinerant magnets. Our approach based on a variational procedure for the free energy generalizes the conventional SF theory to account for anharmonic effects caused by zero-point SF. We show that both aspects of spin anharmonicity, i.e., the variation of the zero-point SF amplitudes and anharmonic effects beyond the weak-coupling approximation are equally important and give rise to the renormalization of the GL parameters defining the ground state and thermal properties.

We emphasize that the thermal properties of itinerant magnets can be interpreted solely in terms of thermally excited SF within, e.g., the quantum GL approach to the SF theory of itinerant magnetism[5] provided the quantum zero-point SF effects are incorporated into the phenomenological GL parameters. This means that the zero-point SF effects may be averaged out basing on the different time scale of the low-frequency thermal and high-frequency zero-point SF. Our work gives the microscopic basis for the phenomenological GL approach, relating the phenomenological parameters to the first-principles band-structure calculations based on the fixed-spin-moment concept.[7,8]

Finally, the above-mentioned general results concerning zero-point fluctuations in ferromagnets may be directly applied to itinerant antiferromagnets, high-T_c superconductors in particular, where SF essentially contribute to neutron scattering.[27] They may also be applied to other fluctuating systems described by the quantum GL model.

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