# Exchange-Coupled Spin-Fluctuation Theory: Application to Fe, Co, and Ni

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(Received 20 December 1995)

Finite-temperature properties are modeled for the itinerant-electron ferromagnets Fe, Co, and Ni by employing a spin-fluctuation theory where the modes are coupled by interatomic exchange interactions. Our method is based on the density functional theory using the local density approximation. The latter yields all parameters derived from constrained ground-state properties of noncollinear spin configurations to calculate *ab initio* the Curie temperatures, the magnetic susceptibilities, and, furthermore, the hcp-fcc phase transition of Co. Our results are in fair agreement with experimental data. [S0031-9007(96)00537-6]

PACS numbers: 71.15.Mb, 75.10.Lp, 75.30.Cr, 75.50.–y

The magnetic properties of transition metals at very low temperatures are well described by spin-polarized band theory provided this is based on the density functional formalism, a rather well-tested computational method being the local density approximation [1,2]. In fact, spin-polarized band theory can be seen as the *ab initio* version of Stoner-Wohlfarth theory [3,4] in which the magnetic moments are brought about by the itinerant *d* electrons whose spins align because of intra-atomic exchange interactions. Recent reviews can be found, e.g., in [5,6].

At finite temperatures, however, Stoner-Wohlfarth theory fails to account for the magnetic properties in most cases, particularly so for Fe, Co, and Ni. The reason for this is that the magnetic moments are supposed to disappear through spin-flip excitations to the Stoner continuum, a process that costs too much energy leading to unphysically high Curie temperatures and a paramagnetic susceptibility that does not describe the experimentally observed Curie-Weiss law.

Awareness of low-energy excitations for explaining the magnetic phase transition arose in the seventies predominantly through the pioneering work of Moriya, Hubbard, Hasegawa, Korenman *et al.*, Gyorffy *et al.*, Edwards [7–12], and others; see, for example, [13,14]. The broad consensus reached [13] was that orientational fluctuations of the local magnetization represent the essential ingredients to a thermodynamic theory. Still, the detailed approaches seemingly differed considerably; thus, for instance, Gyorffy *et al.* [11] emphasized a picture of disordered local moments, whereas Korenman, Murray, and Prange used a fluctuating-local-band picture [10]. In spite of the considerable progress in the formulation of the problem, actual first-principles treatments of spin fluctuations that result in hard numbers for itinerant-electron systems are still rare, a notable exception is given by the work of Staunton and Gyorffy [15].

In this Letter, using an approach different from that of Staunton and Gyorffy, in particular, not making any explicit assumptions about the local degree of order, we obtain first-principles estimates for magnetic properties of 3*d* metals on the basis of ground-state properties using the density functional theory. Assuming the adiabatic approximation for magnetic moments, we separate slow and fast motion, the time scale for spin fluctuations being much longer than typical electronic hopping times. In particular, making the static approximation where the fluctuations are treated classically, we include transverse as well as longitudinal spin fluctuations by using a mode-mode coupling theory. Such a theory was first developed by Murata and Doniach [16] for weakly ferromagnetic systems; it was generalized later [17–20] to apply to a description of magnetic and magnetoelastic properties of itinerant-electron materials. These authors assume the total energy per atom $E$ at $T = 0$ is a function of the magnetic moment $\mathbf{M}$ per atom, $E(\mathbf{M})$, with a ground-state value of $E_0 = E(\mathbf{M}_0)$. Thermal effects are described by random variables $\mathbf{m}(\mathbf{r})$, and $\mathbf{M} = \mathbf{M}_0 + \langle \mathbf{m}(\mathbf{r}) \rangle$ is interpreted as the thermodynamic magnetization, where $\langle \mathbf{m}(\mathbf{r}) \rangle$ is the statistical mean value of the fluctuations $\mathbf{m}(\mathbf{r})$. In a theory reminiscent of a Ginzburg-Landau approach the Hamiltonian is expanded in powers of $\mathbf{M}^2(\mathbf{r})$ where the expansion coefficients can be obtained by constrained calculations of the total energy $E(M)$ [20]. Furthermore, in the limit of weak itinerant ferromagnets, where the angle of the interactions is small in comparison to the scale of the fluctuations, nonlocal effects are taken into account by a lowest-order gradient term, which describes the dispersion of the fluctuations [17,18]. These fluctuations are treated by Fourier-transformed quantities $\mathbf{m}(\mathbf{r}) = \sum_{k<k_c} \mathbf{m}_k \exp(i\mathbf{k} \cdot \mathbf{r})$, where a cutoff parameter $k_c$ is introduced to avoid a divergence of the mean value of fluctuations. The expansion coefficient of the gradient term and the cutoff parameter $k_c$ describe phenomenologically the excitation modes and are fitted to experimental data.

In this work, the gradient term is generalized such that, for the first time, *all* coefficients defining the Hamiltonian are obtained from first principles by total-energy calculations of constrained, noncollinear magnetic configurations. These latter are modeled by means of spin spirals whose intriguing symmetry properties were discussed a long time ago by Herring [21]. Thus the magnetization at site $\mathbf{R}$ is constrained to have the form $\mathbf{M}(\mathbf{R}) = M(\cos(\mathbf{q}\cdot\mathbf{R})\sin\theta, \sin(\mathbf{q}\cdot\mathbf{R})\sin\theta, \cos\theta)$ where $\mathbf{q}$ defines the spiral configuration. Our previously documented ability [22,23] to compute the total energy for these configurations by self-consistent calculations in the local density approximation using the ASW method [24] allows us then to obtain the total-energy "landscape" $E(M,\mathbf{q},\theta)$.

In Fig. 1 the total energy $E(M,\mathbf{q},\theta)$ for Ni is shown as a function of the moment $M$ for different configurations and $\theta = 90°$. Curve FM applies to the ferromagnet [where $\mathbf{q} = (0,0,0)$] with a ground-state energy $E(M_0) = -2.9$ mRy at $M_0 = 0.61\mu_B$, curve SM applies to a spin-spiral configuration where $\mathbf{q} = (0,0,1/2)$, and curve AM applies to the antiferromagnetic configuration where $\mathbf{q} = (0,0,1)$ ($\mathbf{q}$ is given in units of $2\pi/a$ where $a$ is the computed lattice constant). It is important to notice that the AM curve possesses its minimum at the origin, i.e., Ni cannot sustain a magnetic moment in an antiferromagnetic configuration. Indeed, the SM curve shows that starting at about $\mathbf{q} = (0,0,1/2)$, which implies angles of 90° between the spins of nearest neighbors, the magnetic moments vanish. For values of $\mathbf{q}$ slightly smaller than this the total energy possesses a very broad minimum and thus leads to strong spin fluctuations with almost no cost of energy as was pointed out before in calculations of the susceptibility [25]; the situation is similar for fcc-Co the magnetic moments being, however, considerably more stable for bcc-Fe and hcp-Co [25].

We now expand the total energy $E(M,\mathbf{q},\theta)$ in even powers of $M^2$ (only those are needed because of time-reversal symmetry):

$$E(M,\mathbf{q},\theta) = \sum_n A_n M^{2n} + \sum_n J_n(\mathbf{q},\theta) M^{2n}. \qquad (1)$$

Here the first term on the right-hand side describes contributions from collinear ferromagnetic spin configurations and the second term from noncollinear configurations, the latter being expressed by functions $J_n(\mathbf{q},\theta)$ which are proportional to the energy difference between the ferromagnetic and the spin-spiral case and which we, therefore, associate with the exchange energy. The $\theta$ dependence can be shown to be $J_n(\mathbf{q},\theta) \simeq \sin^2\theta J_n(\mathbf{q})$ and, for brevity in writing, we confine ourselves to the leading terms, renaming $A_1 \equiv A$, $A_2 \equiv B$, and $J_1(\mathbf{q}) \equiv J(\mathbf{q})$:

$$E(M,\mathbf{q},\theta) = AM^2 + BM^4 + \sin^2\theta J(\mathbf{q})M^2, \qquad (2)$$

even though the actual calculations were carried out using terms up to $M^8$ which provide a sufficient degree of convergence. The quantities $A$, $B$, and $J(\mathbf{q})$ (plus the higher order corrections) are all we need to carry out the thermodynamic calculations which are described next. Note that this input is in principle temperature dependent. However, for the temperatures of interest (i.e., far below the Stoner continuum that sets the energy scale which for the $3d$ metals is much higher than the Curie temperatures) we expect this dependence to be weak and therefore neglect it.

We now use as the basic Hamiltonian which describes exchange-coupled spin fluctuations the expression

$$\mathcal{H} = \frac{1}{V}\int d^3r[A\mathbf{M}^2(\mathbf{r}) + B\mathbf{M}^4(\mathbf{r}) + \cdots] + \frac{1}{V}\int d^3r \int d^3r'[J(\mathbf{r}-\mathbf{r}')\mathbf{M}(\mathbf{r})\cdot\mathbf{M}(\mathbf{r}') + \cdots], \qquad (3)$$

where $A$ and $B$ are defined above and, contrary to earlier work [16–18], the gradient term is replaced by the more general term containing $J(\mathbf{r}-\mathbf{r}')$. Physically it describes the energy changes due to exchange coupling between the sites $\mathbf{r}$ and $\mathbf{r}'$. The classical field $\mathbf{M}(\mathbf{r})$ is decomposed into the average magnetization $M$—which we define to be along the $z$ direction—and the Fourier modes of the longitudinal ($m_{z\mathbf{k}}$) and transverse ($m_{z\mathbf{k}}, m_{y\mathbf{k}}$) fluctuations:

$$\mathbf{M}(\mathbf{r}) = M\mathbf{e}_z + \sum_{j\mathbf{k}} m_{j\mathbf{k}} \exp(i\mathbf{k}\cdot\mathbf{r})\mathbf{e}_j \qquad (4)$$

and the exchange constants $J(\mathbf{r}-\mathbf{r}')$ are connected with the input quantities $J(\mathbf{q})$ by

$$J(\mathbf{r}) = \frac{1}{V}\sum_{\mathbf{q}} J(\mathbf{q})\exp(i\mathbf{q}\cdot\mathbf{r}). \qquad (5)$$

Since the spin-quantization axis is assumed to be constant inside the atomic sphere [22], the energy $E(M,\mathbf{q})$ is solely composed of exchange integrals $J(\mathbf{R}_i - \mathbf{R}_j)$ between different atomic sites $\mathbf{R}_i$ and $\mathbf{R}_j$, whereas intra-atomic contributions cannot easily be considered. Thus the

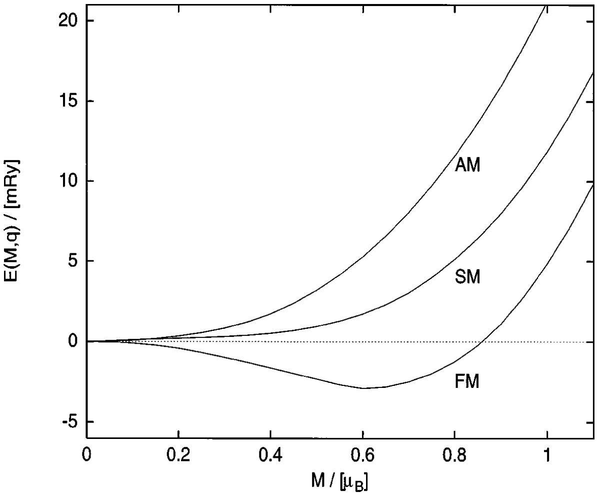

FIG. 1. Total energy $E(M,\mathbf{q})$ in mRy of fcc-Ni as a function of the magnetic moment $M$ in $\mu_B$ for different magnetic configurations: ferromagnet (FM), spin spiral of $\mathbf{q} = (0,0,\frac{1}{2})\frac{2\pi}{a}$ (SM), and antiferromagnet (AM).

exchange constants $J(\mathbf{q})$ are periodic in the reciprocal lattice and the degrees of freedom are the number of different $m_{j\mathbf{k}}$, the wave vectors $\mathbf{k}$ being in the first Brillouin zone. This defines the partition function as $\mathcal{Z} = (\prod_{j,\mathbf{k}\in 1.\mathrm{BZ}} \int dm_{j\mathbf{k}}) \exp(-\mathcal{H}/k_BT)$.

Since the functional integration of the partition function cannot be performed exactly, we resort to a mean-field approximation and obtain the free energy $\mathcal{F}$ as usual by employing the Peierls-Feynman inequality $\mathcal{F} \leq \mathcal{F}_{\mathrm{SF}} = \mathcal{F}_0 + \langle \mathcal{H} - \mathcal{H}_0 \rangle_0$, where the Hamiltonian $\mathcal{H}_0$ is chosen as a quadratic form: $\mathcal{H}_0 = \sum_{j\mathbf{k}} a_{j\mathbf{k}} |m_{j\mathbf{k}}|^2$. Here $a_{j\mathbf{k}}$ are variational parameters and $\mathcal{F}_0$ is the free energy calculated with $\mathcal{H}_0$. Thus the mean value of the fluctuations is simply obtained as $\langle |m_{j\mathbf{k}}|^2 \rangle_0 = k_BT/2a_{j\mathbf{k}}$ and $\langle |m_{j\mathbf{k}}|^{2n} \rangle_0 = (2n-1)!!\langle |m_{j\mathbf{k}}|^2 \rangle_0^n$. We thus calculate the free energy of spin fluctuations, $\mathcal{F}_{\mathrm{SF}}$, as

$$\mathcal{F}_{\mathrm{SF}}(T) = -\frac{k_BT}{2} \sum_{j\mathbf{k}} [1 + \ln(\pi \langle |m_{j\mathbf{k}}|^2 \rangle_0)] + \sum_{j\mathbf{k}} J(\mathbf{k}) \langle |m_{j\mathbf{k}}|^2 \rangle_0 + A(M^2 + 2\tilde{m}_t^2 + \tilde{m}_l^2) \\ + B(M^4 + 4M^2\tilde{m}_t^2 + 6M^2\tilde{m}_l^2 + 8\tilde{m}_t^4 + 4\tilde{m}_t^2\tilde{m}_l^2 + 3\tilde{m}_l^4), \tag{6}$$

where $\langle |m_{t\mathbf{k}}|^2 \rangle_0 = \langle |m_{x\mathbf{k}}|^2 \rangle_0 = \langle |m_{y\mathbf{k}}|^2 \rangle_0$ describe transverse and $\langle |m_{l\mathbf{k}}|^2 \rangle_0 = \langle |m_{z\mathbf{k}}|^2 \rangle_0$ longitudinal fluctuations. Furthermore, the abbreviation $\tilde{m}_j^2 = \sum_{\mathbf{k}} \langle |m_{j\mathbf{k}}|^2 \rangle_0$ is used. Finally, the coefficients $a_{j\mathbf{k}}$ are given by those which minimize the free energy, $\partial \mathcal{F}_{\mathrm{SF}}/\partial a_{j\mathbf{k}} = 0$. These equations constitute the self-consistency condition for the fluctuations $\langle |m_{t\mathbf{k}}|^2 \rangle_0$ and $\langle |m_{l\mathbf{k}}|^2 \rangle_0$ and are

$$\frac{k_BT}{2\langle |m_{t\mathbf{k}}|^2 \rangle_0} = A + B(2M^2 + 8\tilde{m}_t^2 + 2\tilde{m}_l^2) + J(\mathbf{k}), \tag{7}$$

$$\frac{k_BT}{2\langle |m_{l\mathbf{k}}|^2 \rangle_0} = A + B(6M^2 + 4\tilde{m}_t^2 + 6\tilde{m}_l^2) + J(\mathbf{k}). \tag{8}$$

Equations (6), (7), and (8), together with the condition $\partial \mathcal{F}_{SF}/\partial M = 0$, give the temperature dependence of the magnetization as well as of the fluctuations.

Our results for Ni are shown in Fig. 2(a) where we show as a function of the temperature $T$ the magnetization $M$, the fluctuations $\tilde{m}_t^2$, $\tilde{m}_l^2$, and the local magnetic moment $M_S = \sqrt{\langle \mathbf{M}^2(\mathbf{r}) \rangle_0}$. We wish to point out that, due to the quadratic form of $\mathcal{H}_0$, the temperature dependence of the calculated quantities is obtained incorrectly for $T \rightarrow 0$. Also, in some cases—for certain values of the coefficients $A_n$ and $J_n$ of Eq. (1) appropriate for other metals—one obtains a phase transition of first order; see, for instance, [13,19].

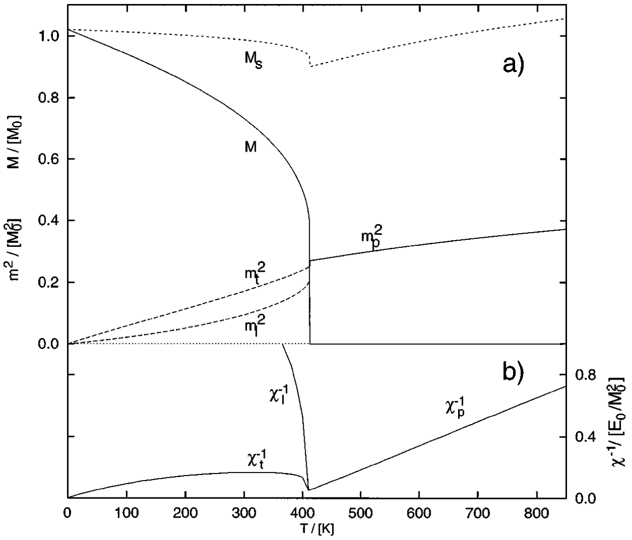

FIG. 2. (a) Relative magnetization $M$, relative transverse and longitudinal fluctuations, $\langle |m_{t\mathbf{k}}|^2 \rangle_0$ and $\langle |m_{l\mathbf{k}}|^2 \rangle_0$ below $T_C$ and $\langle |m_{p\mathbf{k}}|^2 \rangle_0$ above $T_C$, and relative local magnetic moment $M_S$ (see text) for fcc-Ni. (b) Inverse susceptibilities, $\chi_t^{-1}, \chi_l^{-1}$ (for $T < T_C$), and $\chi_p^{-1}$ (for $T > T_C$) of fcc-Ni as a function of the temperature $T$.

From the second derivative of the free energy $\mathcal{F}_{\mathrm{SF}}$ with respect to the fluctuations $m_{j\mathbf{k}}$ we calculate the longitudinal ($\chi_l^{-1}$) and transverse ($\chi_t^{-1}$) susceptibilities below $T_C$ as well as the paramagnetic Curie-Weiss susceptibility ($\chi_p^{-1}$) above $T_C$. Our results are shown in Fig. 2(b). The paramagnetic inverse susceptibility obviously agrees in form with measured results, but the slope is too large by nearly a factor of 2. A similar discrepancy was discussed in [15]. In Table I we collect calculated values of the Curie temperature $T_C$ and the Pauli spin susceptibility $\chi_{00}$ for Fe, Ni, and Co and compare them with experimental results and the calculated values given by Staunton and Gyorffy [15], who obtained their results at high temperatures approaching $T_C$ from above and making assumptions

TABLE I. Calculated saturation magnetizations ($M_0$), Curie temperatures ($T_C$), and Pauli spin susceptibilities ($\chi_{00}$) for Fe, Co, and Ni (calc.). Comparison is with data of Staunton and Gyorffy (SG) [15] and experimental values (exp.) [26]. Also the hcp-fcc phase-transition temperature ($T_{\mathrm{hcp/fcc}}$) of cobalt is given.

| | | bcc-Fe | fcc-Ni | hcp-Co | fcc-Co |
|---|---|---|---|---|---|
| $M_0$ ($\mu_B$) | | 2.20 | 0.61 | 1.52 | 1.61 |
| $T_C$ (K) | Calc. | 1095 | 412 | 995 | 1012 |
| | SG | 1015 | 450 | | |
| | Exp. | 1044 | 627 | | 1388 |
| $\chi_{00}$ ($10^{-6}\frac{\mathrm{emu}}{\mathrm{mol}}$) | Calc. | 56.6 | 38.1 | 63.5 | 118.1 |
| | Exp. | 69–98 | 40–55 | 23–65 | $\cdots$ |
| $T_{\mathrm{hcp/fcc}}$ (K) | Calc. | | | 590 | |
| | Exp. | | | 703 | |

about the local degree of short-range order. Our results for $T_C$ are seen to be in good agreement with experiment for the case of Fe, whereas for the cases of Ni and Co there is a discrepancy of about 30%.

Finally, we might ask if our ability to compute the free energy $\mathcal{F}_{\mathrm{SF}}(T)$ *ab initio* can be used to discuss the hcp-fcc phase transition in Co. By comparing with the fcc structures of Rh and Ir it is common to argue that the hcp structure of Co is stabilized by its being magnetic; indeed, the calculated ground-state energy of ferromagnetic hcp-Co is lower by about 1.7 mRy per atom than that of ferromagnetic fcc Co. Although we cannot definitely rule out other mechanisms like those due to phonons, our calculations lend weight to magnetism as constituting the dominant mechanism. Indeed, only considering spin fluctuations we find the calculated free energy $\mathcal{F}_{\mathrm{SF}}^{\mathrm{hcp}}(T)$ for ferromagnetic hcp-Co to be smaller than $\mathcal{F}_{\mathrm{SF}}^{\mathrm{fcc}}(T)$ for ferromagnetic fcc-Co at low temperatures crossing at a temperature of $T_{\mathrm{hcp/fcc}}^{\mathrm{calc}} = 0.58 T_C^{\mathrm{calc}}$; for temperatures larger than $T_{\mathrm{hcp/fcc}}^{\mathrm{calc}}$ the free energy $\mathcal{F}_{\mathrm{SF}}^{\mathrm{fcc}}(T)$ is lowest up to the Curie temperature where the free energy for *paramagnetic* fcc-Co becomes lowest. The calculated transition temperature $T_{\mathrm{hcp/fcc}}^{\mathrm{calc}}$ corresponds to 590 K, which should be compared with the experimental transition temperature of 703 K [26]. We may conclude that the hexagonal phase of Co at low temperatures is stabilized dominantly by its being magnetic; spin fluctuations and the decreasing magnetization at higher temperatures restore the normal tendency of Co to be face-centered cubic.

In summary, we presented a first-principles theory to describe exchange-coupled spin fluctuations of itinerant-electron systems. In particular, the parameters characterizing the theory are obtained by *ab initio* total-energy calculations of noncollinear spin configurations. Not all configurations result in stable magnetic moments, thus [25] Fe and hcp-Co are barely magnetic for spiral configurations characterized by wave vectors **q** on the Brillouin-zone (BZ) boundary, whereas Ni and fcc-Co lose their moments for even smaller $q$ not exceeding roughly half the radius of the BZ; i.e., angles between the moments of nearest-neighbors cannot exceed 90°. Yet, manifestly, the average local moments above the Curie temperature $T_C$ do not vanish. Having made no assumptions about the degree of local order (in contrast to all previous theories) we thus conclude that these nonmagnetic configurations carry only little weight in the thermodynamics averages and the degree of short-range order must be considerable for Ni and fcc-Co, ruling out disordered local-moment states. This is different for bcc-Fe and hcp-Co where the magnetic moments are found to be much more stable and disordered moment states are conceivable. Our results for $T_C$ and the susceptibilities are in fairly good agreement with experimental values; we therefore state that the local density approximation supplies total-energy surfaces $E(M, \mathbf{q})$ with sufficient precision to encourage a quantitative description of finite-temperature magnetism.

We would like to express our thanks to P. Mohn for interesting and helpful conversations. We are also indebted to L. M. Sandratskii for numerous invaluable discussions. This work was partially supported by the *Deutsche Forschungsgemeinschaft,* SFB 252 Darmstadt, Frankfurt, Mainz.

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