

Magnetic short-range order above the Curie temperature of Fe and Ni

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(Received 26 August 2005; published 13 October 2005)

We report the results of time-dependent density-functional simulations of magnetic properties of Fe and Ni at finite temperatures. They reveal the existence of local moments in Ni above the Curie temperature, coupled to giant magnetic short-range order. In Fe the short-range order is also present to a lesser extent but spin-wave-like propagating and diffusive excitations persist in both materials in the paramagnetic state. The prevailing view of magnetic order in paramagnets should be reconsidered in light of these findings.

DOI: [10.1103/PhysRevB.72.140406](https://doi.org/10.1103/PhysRevB.72.140406)

PACS number(s): 75.50.Bb, 75.10.-b, 75.50.Cc

A proper description of the microscopic behavior of magnetic systems at finite temperature represents one of a few fundamental problems still existing in the theory of magnetism. While numerous model theories with different adjustable parameters lead to some description of magnets at finite temperatures, the attendant approximations significantly influence the final results. *Ab initio* methods have been used since the early 1980's; however, they are limited to zero temperature and largely reproduce the Heisenberg model. As might be expected, such methods provide a good description of magnets with localized moments, but the results for itinerant magnets are rather unsatisfactory. In particular, the temperature dependence of longitudinal fluctuations and magnetic short-range order (MSRO) have always been neglected.

MSRO in itinerant magnets is the subject of a long-standing controversy. Early reports on inelastic neutron-scattering experiments indicated the persistence of spin-wave-like modes with relatively small wave vectors above the Curie temperature T_c in both Ni and Fe (Ref. 1). Based on these results, the local band theory was developed,² but its assumptions are incompatible with the observed Curie-Weiss susceptibility and specific-heat anomaly.³ Since then, various experiments⁴ confirm the presence of some degree of MSRO in many ferromagnets, and the present belief is that it can be very strong. However, up to now theory has failed to estimate the degree of MSRO in different magnets, owing to the formidable challenges in implementing a tractable theory for real materials.

Several quantitative theoretical methods based on the use of the calculated band structure have been developed. In many cases the *ab initio* version of the single-site coherent potential approximation (CPA) was employed. The first calculation⁵ evaluates the MSRO in Fe by calculating the nonlocal exchange coupling. However, the single-site CPA presupposes that MSRO is absent; hence the calculated MSRO is small. Further CPA calculations⁶ also obtained a good description of finite-temperature properties of bcc Fe, but do not find any local magnetic moment (LMM) at high temperatures in fcc Ni. Using Onsager's reaction-field approach,⁶ the description of Ni can be improved, which indicates that some interatomic correlations beyond the mean-field approximation (MFA) should be included, at least for Ni.

Different tight-binding methods not based on the CPA

have been used to estimate the MSRO and the effective coupling in Fe and Ni (Ref. 7). Most did not find strong MSRO and failed to explain the corresponding experimental data. In Ref. 8 it was claimed that the effective coupling is much stronger at the Curie temperature than at $T=0$, which makes the temperature dependence of the exchange coupling a very important problem. However, as we will discuss below, the tight-binding approximation leads to a strong underestimation of MSRO, and hence to different physics. The first band-structure calculations of the effective exchange coupling² may be regarded as being in the limit, which is opposite to the CPA, since the local band theory assumes strong MSRO. However, these calculations⁹ yielded a much smaller degree of MSRO in contradiction with the initial assumption. Thus, it seems that no numerical calculations so far have explicitly shown the presence of strong MSRO in Fe or Ni based on their band structures, while the experiments clearly indicate its presence.

The second key point concerns the proper inclusion of longitudinal fluctuations in itinerant magnets at finite temperature, which are missing in any random-phase approximation (RPA) theory.

If it were not for serious challenges limiting its tractability, density functional spin dynamics would be a very powerful tool to address all these issues. In Ref. 10 a combination of first-principles spin dynamics with different stochastic or deterministic types of finite-temperature description was proposed. Below we present an implementation that makes this technique practicable, and apply it for the first time to studies of finite-temperature behavior of ferromagnetic Fe and Ni. This approach is based on time-dependent spin-density-functional theory.¹¹ The main equation in this theory is

$$i \frac{\partial \psi}{\partial t} = \left(-\nabla^2 + V(\mathbf{r}) - \frac{1}{2} [\mathbf{B}_{xc}(\mathbf{r}) + \mathbf{B}_{ext}(\mathbf{r})] \sigma \right) \psi, \quad (1)$$

where $V(\mathbf{r})$ is a nonmagnetic part of the total potential, $\mathbf{B}_{xc}(\mathbf{r})$ is the magnetic part of the exchange correlation potential, and $\mathbf{B}_{ext}(\mathbf{r})$ is the external magnetic field.

Instead of considering the evolution of the nonlocal density matrix, one can introduce the closed system of coupled equations for the three local one-electron quantities: the charge density $n_\nu(\mathbf{r}, t)$, the magnetization density $\mathbf{m}_\nu(\mathbf{r}, t)$,

and the velocity density $\mathbf{v}_v(\mathbf{r}, t)$. Separating the magnetization dynamics adiabatically, one can obtain the main one-electron equation of spin dynamics

$$\frac{d\mathbf{m}_v}{dt} = \gamma \mathbf{m}_v \times [\mathbf{B}_v^{kin}(\mathbf{r}, t) + \mathbf{B}_{xc}(\mathbf{r}, t) + \mathbf{B}_{ext}(\mathbf{r}, t)], \quad (2)$$

where $\mathbf{B}_v^{kin}(\mathbf{r}) = \nabla(n_v \nabla \mathbf{m}_v) / n_v$, $d/dt = \partial/\partial t + \mathbf{v}_v \nabla$, and \mathbf{v}_v is the velocity field for the electron liquid.

The basic assumption of the local spin-density approximation (LSDA) is that the exchange-correlation potential of the homogeneous electron gas with fixed charge density n and magnetization density \mathbf{m} can be applied to real external potentials. In this approximation $\mathbf{B}_{xc}(\mathbf{r}) \uparrow \uparrow \mathbf{m}(\mathbf{r})$, and hence assumes very strong exchange-correlation field $\mathbf{B}_{xc}(\mathbf{r}, t)$ compared to the “kinetic” field $\mathbf{B}^{kin}(\mathbf{r}, t)$ and the smallness of dynamics associated with the exchange-correlation term. This approximation assumes that correlation effects do not contribute to the spin dynamics of magnets, but attributes all of the dynamics to the kinetic term. Many static calculations of spin excitations have generally confirmed that this approximation is valid for many materials. In Ref. 12 we estimated the strength of correlation effects by calculating the contribution of nonlocal Coulomb correlations to the spin-wave stiffness. This contribution happened to be very small compared to the kinetic contribution. Below we will confirm that this approximation is quite reasonable for dynamic simulations as well.

In this paper we solve Eq. (2) by using the classical Langevin approach for finite temperatures, and employ the so-called orbital dynamics approach¹⁰ so that each orbital can precess with its own frequency, independent of the other orbitals. In this treatment we avoid the standard adiabaticity which is assumed in the dynamic rigid spin approximation, and account for all decoherence effects properly within LSDA. This approach is similar to the linear-response technique when the external field is small. However, our approach does not necessarily assume that the *perturbation* is small.

All calculations were performed within LSDA using the tight-binding linear muffin-tin orbital method. In typical calculations with 100–120 atoms per cell we used 20–30 k points in the irreducible part of the Brillouin zone. The correct description of possible long-range magnetic order (especially at low temperatures) requires that the simulation cell contains many atoms. To avoid this numerical difficulty, we added temperature- and time-dependent spin-spiral boundary conditions,¹³ with its corresponding equation of motion. Similar to the static case, such combined real and/or reciprocal-space spin dynamics allowed us to significantly reduce the number of atoms per cell in our simulations and made numerous statistical calculations possible. From the physical point of view, the simultaneous inclusion of real-space short-range modes (inside the supercell) and long-wavelength modes (between supercells) enables the description of magnetic excitations developing at different length scales, as well as their interactions, on an equal footing.

First, let us discuss static properties. In Fig. 1 we show the total magnetization of Fe as a function of temperature. The

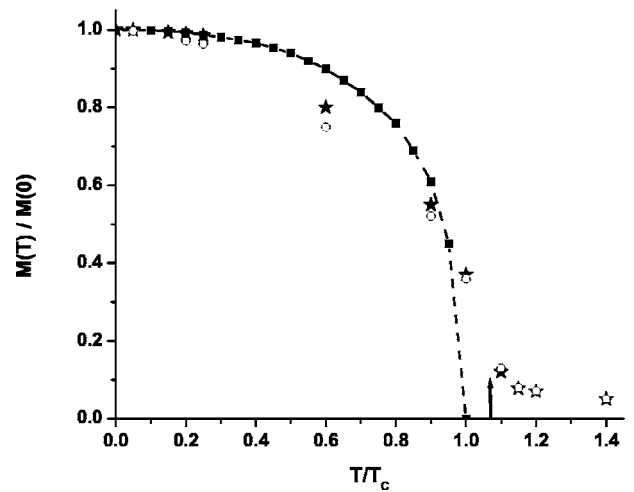


FIG. 1. Magnetization of bcc Fe as a function of temperature obtained for the simulation cell containing 128 atoms with dynamic spin-spiral boundary conditions. The filled stars (★) and open circles (○) correspond to orbital and rigid spin approximation spin dynamics, respectively. The closed squares (■) show experimental data. The arrow indicates the finite-size scaling result for the Curie temperature of Fe.

results for the 128-atom simulation (using dynamical spin spiral boundary conditions) for Fe are shown together with the finite-size scaling results. The finite-size scaling results were obtained using supercells of four different sizes for both Ni and Fe. The effectiveness of the dynamical spiral boundary conditions can be seen in the 128-atom simulation. The low magnetization “tail” above T_c was reproduced in standard real-space calculations (Monte Carlo simulations for the Heisenberg model) only when 7000–8000 atoms were used.¹⁴ T_c resulting from the simulation is quite satisfactory. For Fe, nearly perfect agreement with experiment is obtained: 1070 K (1023 K); in Ni T_c is about 25% smaller than experiment: 470 K (623 K). However, this discrepancy may be attributed to the LSDA itself: the total-energy difference between fully ferromagnetic and nonmagnetic Ni is about 550 K (with all parameters identical to the dynamical simulation). While this upper limit to the T_c in Ni is somewhat higher when gradient corrections are added to LSDA, we do not have presently a sufficiently accurate density functional to disentangle the LSDA contribution from the error. We only suggest that this error is connected with some on-site Coulomb correlations which are missing in LSDA at $T = 0$ K. The proper account of quantum corrections could significantly affect T_c as well.

The effective paramagnetic moment p_c was extracted from the calculations of high-temperature susceptibility. These moments compared to experimental values¹⁵ are 3.3 (3.13) and 1.75 (1.6) Bohr magnetons for Fe and Ni, respectively.

To interpret these large moments we will now discuss the dynamical properties. A very unusual picture of magnetic order near T_c emerges. The crucial physical quantity which reveals a degree of short- or long-range order in magnets is the spin-spin correlation function

$$S_{ij} \sim \langle \langle \mathbf{m}_i(t) \mathbf{m}_j(t') \rangle \rangle, \quad (3)$$

where $\langle \langle \dots \rangle \rangle$ indicates the thermodynamic average. The short-range part of S_{ij} is strongly affected by the presence of itineracy in the magnetic system. The analysis of S_{ij} shows that the average angle between nearest neighbors' LMM is 67° in bcc Fe near T_c , however in fcc Ni it is just 28° . These numbers are very stable as a function of temperature: within a temperature range of $0.95T_c - 1.05T_c$ their overall changes do not exceed 3–4 %. The deviation from 90° indicates that in Fe the MSRO is relatively small (but noticeable), while in Ni it is enormous. A real-space analysis of the correlation function shows that in Ni the dynamic ordering is of the spin-spiral or domain-wall type, with a period of ~ 14 a.u. On the other hand, in Fe nearest-neighbor correlations dominate and a relatively weak superparamagnetic-type MSRO is realized at T_c . Overall, the dynamic correlation function has very well-defined peaks well above T_c and clearly demonstrates the persistence of the spin-wave-like diffusive ($Q=0$) and propagating (finite Q) perturbations in the paramagnetic state of Fe and Ni. The relatively high energy of short-wave ferromagnons in these materials is primarily responsible for this feature.

The presence of such MSRO at T_c also indicates that the nearest-neighbor interactions in these materials must be larger than T_c . However, the exchange couplings in these materials are well known (see Refs. 9 and 16) and corresponding numbers are somewhat lower than T_c , making the existence of the strong MSRO in these materials questionable. On the other hand, starting from pioneering calculations in Ref. 9 all calculations of J_{ij} assumed a long-wave approximation (LWA) which has a smallness parameter $\Delta \approx J_{ij}/I$, where I is the Stoner parameter.¹⁷ In general, this approximation is inapplicable to systems with strong interatomic interactions (as in the case of itinerant magnets). We found that the usage of the more general definition ($J = \chi^{-1}$) leads to a much better interpretation of our results. First of all, the LWA is suitable for a relatively “localized” system such as Fe, and the corresponding change in the nearest-neighbor exchange is relatively small ($\sim 15\%$). Ni represents a rather itinerant system, and any local approach (especially LWA) is expected to produce a large error. In our case, J_{01} for Ni is increased by more than three times relative to the LWA, indicating that the effective coupling is much larger than T_c . These results explain why the MSRO was missed in previous calculations of J_{ij} and indicate that the traditional MFA (or any other approach that is based on the assumption of “no short-range order”) is inapplicable to itinerant systems in general, predicting very high T_c (above 1000 K in Ni). This interpretation has a qualitative character due to known violation of adiabaticity criteria in the itinerant magnets.

The MSRO allows us to provide a different interpretation of the susceptibility results as described above. The increase of the effective magnetic moment p_c in the Curie-Weiss law compared to the localized model is directly related to clustering (for example, of the superparamagnetic type) when the effective moment of the cluster is several times larger than the original atomic moment. The ratio of the effective moment to the atomic moment is larger in Ni than in Fe. Our

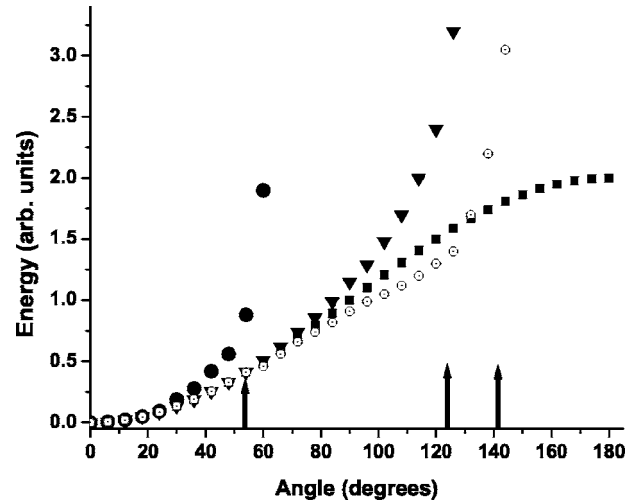


FIG. 2. Total energy as a function of angle between the magnetic moment of a single isolated impurity and the global bulk magnetization. The closed circles (●) correspond to a Ni impurity in fcc Ni; triangles (▼), to a Fe impurity in bcc Fe; open circles (○), to a Ni atom with the relaxation of its nearest neighbors included. A function $(1 - \cos \theta)$ is also shown by squares. The energy is normalized by the stiffness of the corresponding problem. The arrows indicate the “critical” angles where the local moment on the given impurity disappears.

calculations also indicate that in Ni a significant contribution (15%) comes from longitudinal fluctuations. The high-temperature paramagnetic state of Ni has both tangential and longitudinal modes as soft modes which are much closer to each other than at $T=0$ K. We performed several model calculations for Ni assuming static disorder with a 90° average angle between nearest LMM (no MSRO). For all eight random configurations studied, the value of p_c was much lower (about 50–60 % of our theoretical value), clearly supporting MSRO contribution to the p_c . In addition, all final self-consistent states in Ni for these random configurations appeared to be nonmagnetic. So, we believe that strong MSRO is a requirement for fcc Ni to be ferromagnetic and a similar conclusion should apply to all itinerant magnets.

Such strong MSRO cannot appear only at finite temperatures; it must exist already at $T=0$ K (as indicated by our calculations of the effective coupling). To study MSRO in more detail we performed the following model calculations at $T=0$ K. First, we studied the degree of MSRO by rotating the LMM at one site by an arbitrary angle (similar to Ref. 18 but with LWA removed). In the case of the fully localized Heisenberg type of interaction one can expect that such perturbation is stable and the total energy is described by $(1 - \cos \theta)$ type of behavior. Our calculation revealed a completely different picture (Fig. 2). In the case of single-site perturbation, the atomic magnetic moment in Fe disappears at approximately 120° . Longitudinal fluctuations at this point become so important that the moment is inverted. As we mentioned above, such effects cannot be described in any tight-binding type of approach. In Ni the situation is even more complicated and at $\sim 50^\circ$ the local moment is completely destroyed. These calculations immediately suggest that spin dynamics of both Fe and Ni exist in very limited

phase space. We also found that the LMM with opposite spin configuration in bcc Fe can be stabilized if the perturbation is extended to the first shell of neighboring atoms, providing a clear range of minimal MSRO to support such strong local perturbation. In the itinerant Ni the complete flip of LMM cannot be stabilized even if the perturbation is extended to the first-neighboring atoms (Fig. 2). The perturbation is stabilized only when it is extended to three shells of neighbors. These calculations strongly support the idea of giant MSRO in fcc Ni and relatively small (but essential) MSRO in bcc Fe.

Another indication of itineracy (and strong MSRO) was obtained from studies of nonmagnetic configurations. We estimated the range of existence of LMM in nonmagnetic fcc Ni. In the case when LMM exists only at one atom such fluctuation is unstable and LMM simply does not exist. However, if the LMM is fixed at its equilibrium value ($0.6\mu_B$) on nearest atoms, the atomic LMM is stable. According to our LSDA calculations, fcc Ni at its experimental density has stable LMM of $\sim 0.6\mu_B$ only if it has ferromagnetic interaction with two nearest shells of atoms with the same moments. This result clearly indicates that magnetism in Ni has itinerant character. Its nature in this material is not so much in intra-atomic interactions but rather in interatomic ferromagnetic interactions with nearest neighbors. This also indicates that the standard adiabatic criterion is not applicable in Ni at finite temperatures.

Such strong MSRO also allows us to resolve a very old issue of the importance of quantum corrections for T_c and high-temperature susceptibility calculations. These corrections are traditionally small in the localized systems ($4f$ magnets), but always considered to be significant in the itinerant systems. MSRO described above also strongly suppresses quantum corrections in the case of the itinerant magnets by

increasing the effective moment and limiting usual quantization phase space.

In summary, we performed spin-dynamic simulations at finite temperatures using time-dependent spin-density-functional theory. Our calculations revealed the existence of magnetic short-range order at T_c in $3d$ ferromagnetic magnets Fe and Ni. This short-range order is relatively small in bcc Fe (the average angle between local magnetic moments $|\theta| \sim 70^\circ$), while in fcc Ni it is rather large ($|\theta| \sim 25^\circ$). The existence of “distorted” propagating and diffusive spin waves above T_c significantly reduces the range of applicability of the traditional models of magnetism which are based on the idea of the spin wave disappearing at T_c , and demonstrates that more reliable models of magnetism are needed. This MSRO strongly affects all observable properties and establishes that the thermodynamics of Fe and Ni can be described in the framework of the density-functional approach. We believe that MSRO is a natural property of any magnet over a very wide temperature range and is the *sine qua non* in low moment ($m < 2\mu_B$) itinerant magnets where MSRO dramatically influences thermodynamical properties. This MSRO is unique in each system and has a certain “memory” about the ground state of that system. From the methodical point of view the successful usage of our approach clearly indicates that the kinetic energy produces the largest contribution to the dynamics of magnets at finite temperature while the exchange-correlation contribution is small.

This work was carried out at the Ames Laboratory, which is operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-82. This work was supported by the Director for Energy Research, Office of Basic Energy Sciences of the U.S. Department of Energy.

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