Finite-temperature properties of frustrated classical spins coupled to the lattice

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We present extensive Monte Carlo simulations for a classical antiferromagnetic Heisenberg model with both nearest (\(J_1\)) and next-nearest (\(J_2\)) exchange couplings on the square lattice coupled to the lattice degrees of freedom. The Ising-like phase transition, that appears for \(J_2/J_1 > 1/2\) in the pure spin model, is strengthened by the spin-lattice coupling, and is accompanied by a lattice deformation from a tetragonal symmetry to an orthorhombic one. Evidences that the universality class of the transition does not change with the inclusion of the spin-lattice coupling are reported. Implications for \(\text{Li}_2\text{VOSiO}_4\), the prototype for a layered \(J_1-J_2\) model in the collinear regime, are also discussed.

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I. INTRODUCTION

The role of frustrating interactions in low-dimensional systems is a very important aspect in the modern theory of magnetism in solids and molecular clusters. In particular, the presence of finite-temperature phase transitions in two-dimensional systems with continuous spin-rotational symmetry, that are ruled out by a naive interpretation of the Mermin and Wagner theorem, has been clearly documented during the last years and continues to attract much attention, because of the variety of phenomena that could be generated at low temperature. The main point is that the presence of frustrating interactions can induce non-trivial degrees of freedom, that may undergo a phase transition when the temperature is lowered. Among the strongly frustrated spin systems, probably one of the most important examples is the antiferromagnetic Heisenberg model on the square lattice with both nearest (\(J_1\)) and next-nearest neighbor (\(J_2\)) couplings, for which it has recently become certain that a very interesting scenario shows up for large enough frustrating ratio \(J_2/J_1\). Indeed, for \(J_2/J_1 > 1/2\) and classical spins, the two sublattices are completely decoupled at zero temperature, and each of them has an independent antiferromagnetic order. Therefore, the ground-state energy does not depend on the relative orientation between the magnetizations of the two sublattices and the ground state has an \(O(3)\times O(3)\) symmetry. At low temperature, thermal fluctuations lift this huge degeneracy by an order by disorder mechanism\(^{7}\) and two families of collinear states are entropically selected, with pitch vectors \(\mathbf{Q} = (0, \pi)\) and \((\pi, 0)\), respectively. Chandra, Coleman, and Larkin\(^{8}\) argued that this fact reduces the symmetry to \(O(3)\times Z_2\), and that the \(Z_2\) symmetry is broken at low temperature, giving rise to an Ising-like phase transition at finite temperature. Recently\(^{6}\) it has been possible to verify this scenario by using extensive Monte Carlo simulations, and a rather accurate estimate of the critical temperature as a function of the ratio \(J_2/J_1\) has been obtained.

The fact that the two states with \(\mathbf{Q} = (0, \pi)\) and \((\pi, 0)\) break the rotational symmetry, having antiferromagnetic spin correlations in one spatial direction and ferromagnetic correlations in the other, suggests that, once the spin-lattice coupling is considered, the lattice could also experience a phase transition, ferromagnetic and antiferromagnetic bonds acquiring different lengths. Indeed, on general grounds, the super-exchange couplings come from a virtual hopping of the electrons, which depends upon the actual distance of the ions. A first evidence that a similar distortion of the lattice appears when the spins are coupled to classical lattice distortions has been found in Ref.\(^{1}\), where the quantum \(J_1-J_2\) model at zero temperature has been analyzed by Lanczos diagonalization on small clusters. In particular, by considering a \(4 \times 4\) lattice and spin-1/2 coupled to adiabatic phonons, it has been shown that there is a large region where the lattice distorts and ferromagnetic and antiferromagnetic bonds acquire different lengths.

Interestingly, there is also clear evidence that such a scenario is realized in a real compound, \(\text{Li}_2\text{VOSiO}_4\), a vanadate which can be considered as a prototype of the \(J_1-J_2\) model in the collinear region.\(^{12,13}\) Indeed, although the value of \(J_2/J_1\) is not exactly known,\(^{13,14,15}\) all estimates indicate that \(J_2 \gtrsim J_1\). Moreover, NMR and muon spin rotation magnetization provide a clear evidence for the presence of a phase transition to a collinear order at \(T_c \sim 2.8K\) and a structural distortion at a nearby temperature. A simple and appealing explanation relies on the existence of the Ising-like transition and the concomitant lattice distortions.

Since an unbiased finite-temperature analysis of the quantum model for large clusters is, at present, impossible, in this work we would like to address the simpler problem of classical spins coupled to lattice distortions. Although this could be viewed as a crude approximation...
to the original quantum model, especially for low temperature and near the disordered region (expected near \( J_2/J_1 \approx 1/2 \)), the classical case of spins coupled to lattice deformation represents a highly non-trivial problem and, certainly, gives the zeroth-order approximation for the true quantum case.

The paper is organized as follows: In Sec. II we present the model and the method used and in Sec. III we show the results and draw the conclusions.

II. THE MODEL AND THE METHOD

In this section we introduce the spin-lattice Hamiltonian and briefly describe the method we used to treat the lattice degrees of freedom. The Hamiltonian reads:

\[
\hat{H} = \sum_{\langle i,j \rangle} J_1(d_{ij}) \hat{S}_i \cdot \hat{S}_j + \sum_{\langle\langle i,j \rangle\rangle} J_2(d_{ij}) \hat{S}_i \cdot \hat{S}_j + \frac{K_1}{2} \sum_{\langle i,j \rangle} \left( \frac{d_{ij} - d_{ij}^0}{d_{ij}^0} \right)^2 + \frac{K_2}{2} \sum_{\langle\langle i,j \rangle\rangle} \left( \frac{d_{ij} - d_{ij}^0}{d_{ij}^0} \right)^2
\]

(1)

where \( \hat{S}_i \) are O(3) spins on a periodic square lattice with \( N = L \times L \) sites. \( \langle i,j \rangle \) and \( \langle\langle i,j \rangle\rangle \) indicate the sum over nearest and next-nearest neighbors, respectively. The super-exchange couplings \( J_1(d_{ij}) \) and \( J_2(d_{ij}) \) depend upon the distance \( d_{ij} \) of the sites \( i \) and \( j \), and \( K_1 \) and \( K_2 \) are the elastic coupling constants. Finally, \( d_{ij}^0 \) is the bare lattice distance. In transition metal compounds, general arguments lead to exchange integrals that vary like the inverse of the distance to a certain power \( \theta \), with \( \theta \) in the range 5–15. Therefore, for small displacements around the equilibrium positions, we can write:

\[
J(d_{ij}) = J \left( \frac{d_{ij}^0}{d_{ij}} \right)^\theta \approx J \left[ 1 - \theta \left( \frac{d_{ij} - d_{ij}^0}{d_{ij}^0} \right) \right].
\]

(2)

In the Hamiltonian of Eq. (1), we treat both the spins \( \hat{S}_i \) and the lattice coordinates \( d_{ij} \) as dynamical variables, allowing them to change their configurations. With respect to the pure spin problem, this fact doubles the number of dynamical variables present in the problem and makes the Monte Carlo algorithm much heavier. In particular, we find better to use Monte Carlo algorithms with local and/or global updates, instead of more involved Monte Carlo methods based on the reconstruction of the density of states \( N^\uparrow \) that we used in the case where the lattice is kept fixed.

In practice, we work on a torus with two independent lengths \( L_x \) and \( L_y \), which play the role of additional degrees of freedom sampled by Monte Carlo. Moreover, each site of the cluster can independently change its position in the lattice. These facts allow us to consider structural distortions as well as the usual spin properties. We found that, besides small displacements around their equilibrium positions, the sites always form either a square cluster, with tetragonal symmetry and equal lattice spacing, \( l_x \) and \( l_y \), in the two spatial directions (i.e., \( l_x = l_y \)) or a rectangular cluster, with orthorhombic symmetry and different lattice spacings in the two directions (i.e., \( l_x \neq l_y \)). In these cases the total lengths of the cluster in the two directions are \( L_x = L \times l_x \) and \( L_y = L \times l_y \).

For the pure spin model, e.g., with fixed distances and \( J(d_{ij}) = J \), in order to characterize the Ising-like phase transition, it is useful to construct from the original spin variables \( \hat{S}_i \), an effective Ising variable (on the dual lattice)

\[
\sigma_x = \frac{\langle \hat{S}_i - \hat{S}_k \rangle \cdot \langle \hat{S}_j - \hat{S}_l \rangle}{|\langle \hat{S}_i - \hat{S}_k \rangle \cdot \langle \hat{S}_j - \hat{S}_l \rangle|},
\]

(3)

where \( (i,j,k,l) \) are the corners with diagonal \( (i,k) \) and \( (j,l) \) of the plaquette centered at the site \( x \) of the dual lattice. In this way, the two collinear states with \( \mathbf{Q} = (\pi,0) \) and \( \mathbf{Q} = (0,\pi) \) can be distinguished by the value of the Ising variable, \( \sigma_x = \pm 1 \). As emphasized in Ref. 7, the normalization term does not affect the critical properties of the model and it is only introduced to have a normalized variable.

Moreover, we can easily construct the Ising-like order parameter as \( M_x = (1/N) \sum_x \sigma_x \). Associated to the Ising magnetization \( M_x \), we can define the susceptibility related to the Ising variable \( \chi = (N/T)((M_x^2) - (|M_x|)^2) \). Finally, in order to study the finite-temperature phase diagram, it is also useful to consider the specific heat per
site $C_{\sigma} = (1/\Omega T^2)(\langle E^2 \rangle - \langle E \rangle^2)$, $E$ being the total energy of the system.

Before considering the Monte Carlo results at finite temperature, it is useful to discuss the zero-temperature phase diagram of the spin-lattice Hamiltonian of Eq. (1), see Fig. 1. In this case, the first-order phase transition present for $\theta = 0$, i.e., for the pure spin model, at $J_2/J_1 = 0.5$ bends towards smaller values of the frustrating ratio $J_2/J_1$ when the coupling to the lattice is switched on. In particular, the huge $O(3) \times O(3)$ degeneracy is already broken at zero temperature, and the collinear states with pitch vector $Q = (\pi, 0)$ and $Q = (0, \pi)$ have a lower energy. It is worth noting that this is a general property of the spin-lattice coupling, which is also present in the quantum case. Therefore, on the basis of the analysis presented in Ref. 7, in the presence of the spin-lattice coupling, we expect that a finite-temperature phase transition shows up also for a bare ratio $J_2/J_1 < 1/2$, whenever the coupling $\theta$ is sufficiently large, i.e., $\theta > \theta_c$. In the following, we will present strong evidences that there is a finite-temperature phase transition that is related to a change in the lattice symmetry, from a high-temperature disordered magnetic phase with a tetragonal lattice to a low-temperature Ising-ordered phase, with $M_{\sigma} \neq 0$, and with an orthorhombic lattice. A little bit more subtle is the determination of the universality class of this transition. By using powerful Monte Carlo methods, we showed that, in the absence of spin-lattice coupling, the transition belongs to the Ising universality class as expected from more general arguments. The concomitant presence of spin and lattice degrees of freedom makes the Monte Carlo calculation much heavier than in the simpler case where only spins are considered, and we are limited to smaller clusters. Nevertheless, we can reach rather large lattices, that enable us to have convincing results for the thermodynamic limit.

### III. RESULTS AND DISCUSSION

In this section, we present the Monte Carlo results for the Hamiltonian of Eq. (1), and we give evidences that the Ising transition present in the pure spin model survives when the spin-lattice coupling is taken into account, and, moreover, that it is accompanied by a structural deformation.

As discussed in the previous section, in the presence of both spin and lattice degrees of freedom, the Monte Carlo simulations become rather expensive and we are limited concerning the size of the clusters. In order to have a sufficiently high transition temperature $T_c$, that allows a reliable estimate of the physical properties, most of the calculations have been performed for $J_2/J_1 = 0.8$ and three different values of the spin-lattice coupling, $\theta = 5$, 10, and 15 for $K_1 = K_2 = K$. In the following we consider the case of $K/J_1 = 100$. Then, we also report calculations for other values of the ratio $J_2/J_1$, where a similar behavior is observed. Therefore, on the basis of our numerical results, we argue that different choices for the frustrating ratio $J_2/J_1$ or for the elastic coupling $K_1$ and $K_2$ do not change qualitatively the physical behavior of the system. However, it should be emphasized that a precise determination of the critical exponents could be difficult and, in general, rather large clusters are needed. In the following, we present evidences that the transition belongs to the Ising universality class, which has been clearly documented in the absence of spin-lattice coupling.
The size dependence of the spin susceptibility is not affected by the spin-transition. It is worth noting that, while the maximum marks the presence of a phase transition, for which \( V_{\text{max}}(L) \sim L^2 \) and \( C_{\text{max}}(L) \sim L^2 \). As clearly shown for \( \theta = 0.2 \), when the spins are completely decoupled from the underlying lattice, the phase transition is second order and falls into the Ising universality class, i.e., \( \alpha = 0, \nu = 1 \) and \( \gamma = 7/4 \). In this case, an accurate determination of \( \alpha \) is quite hard and rather large clusters are needed (i.e., \( L \sim 200 \)). In the case of a finite \( \theta \), we cannot afford such large clusters, but, nevertheless, we can obtain rather convincing evidences in favor of the Ising universality class by considering the case of a large spin-lattice coupling \( \theta \). Indeed, in Fig. 4 we show the size scaling of the maximum of the specific heat and of the spin susceptibility for \( \theta = 15 \). As mentioned above, the value of the peak of the susceptibility does not depend upon \( \theta \), and, therefore, the results are also valid for other values of the spin-lattice couplings. A three-parameter fit of \( \chi_{\text{max}}(L) = a + b \times L^{\gamma/\nu} \) gives \( \gamma/\nu = 1.7 \pm 0.1 \), which is in reasonable agreement with the value 1.75 of the Ising transition. Moreover, the clearest evidence that the transition belongs to the Ising universality class comes from the specific heat. Indeed, the best fit of the maximum of the specific heat is given by \( C_{\text{max}}(L) = a_0 + a_1 \log(L) + a_2/L^{20/3} \), while a power law turns out to be completely inadequate. This fact completely rules out the possibility to have a first-order phase transition, for which a power law with an exponent \( \alpha = 2 \) is expected. For smaller values of \( \theta \) it is much harder to get an accurate fit of \( C_{\text{max}}(L) \), and much larger sizes should be considered. Nevertheless, having in mind the results for \( \theta = 0 \), we expect that the phase transition also falls into the Ising universality class for small spin-lattice couplings.

By using a similar analysis for different \( J_2/J_1 \), it is possible to determine the behavior of the critical temperature \( T_c \) as a function of the frustrating ratio \( J_2/J_1 \) for different values of \( \theta \). The results are reported in Fig. 5. In particular, in order to determine \( T_c \), we used two alternative methods that give consistent results: On one hand, we take the temperatures for which the susceptibility has its maximum and we make use of the scaling \( T_c(L) \sim T_c + a \times L^{-1} \) (which assumes \( \nu = 1 \)); on the other hand, we used Binder’s fourth cumulant of the Ising parameter. Interestingly, as already anticipated, for a sufficiently large value of the spin-lattice coupling there is a phase transition to a collinear phase even if \( J_2/J_1 < 1/2 \) as soon as the spin-lattice coupling is switched on, the critical ratio \( J_2/J_1 \) for which a transition occurs for a given \( \theta \) being in good agreement with the static analysis (Fig. 6).

Now, we turn to the discussion of the lattice properties. Because the two families of states with pitch vectors \( Q = (0, \pi) \) and \( (\pi, 0) \), that are entropically selected, have different spin correlations in the two spatial directions, whenever the sites of the lattices are coupled to the spins, a structural transition is also likely to show up. Indeed, while at high temperature the lattice has a tetragonal symmetry, with the same lattice spacing in the...
FIG. 5: Upper panel: Size scaling of the maximum of the specific heat as a function of the size of the cluster for $\theta = 15$. Lower panel: The same for the maximum of the spin susceptibility. In both cases, the dashed line is a three-parameter fit (see text).

FIG. 6: The critical temperature $T_c$ as a function of the frustrating ratio $J_2/J_1$ for three different values of the spin-lattice couplings, $\theta = 5$, 10, and 15. The case for the pure spin model, corresponding to $\theta = 0$, is also reported for comparison.

$\theta$ and $\sigma$ directions, at the transition temperature, the lattice undergoes a structural phase transition towards an orthorhombic symmetry, with different lattice spacings $l_x$ and $l_y$, see Figs. 7 and 8. This is exactly equivalent to what happens at zero temperature in the quantum case, where the collinear phase is also accompanied by a lattice distortion. Notice that, since we are considering classical spins, the only relevant distortion is the orthorhombic one, and, indeed, we do not find any evidence towards other displacements of the underlying lattice, in contrast to the spin 1/2 case.11

One important outcome is that the structural phase transition has a huge effect just below the critical temperature. Indeed, the lattice displacements strongly stabilize one of the two families of states, and almost freeze the spin fluctuations. This can be clearly seen from the Ising-like magnetization $M_\sigma$, whose value is practically fixed to its saturation value from zero temperature up to $T_c$, where it goes to zero (or to a very small value for finite sizes), see Figs. 7 and 8.

FIG. 7: Upper panel: lattice parameters $l_x$ and $l_y$ as a function of the temperature for $\theta = 5$ for $L = 20$ and 80. Lower panel: The same for the Ising magnetization $M_\sigma$.

FIG. 8: The same as in Fig. 7 for $\theta = 10$. 
The implications for quasi-two-dimensional models with inter-plane magnetic couplings will presumably depend on the value of this coupling. If it is sufficiently weak, we expect the system to undergo two phase transitions: First, coming from high temperature, an Ising like transition involving a lattice distortion and a breaking of the rotational symmetry of spin fluctuations, then a three-dimensional magnetic ordering. However, since the correlation length increases exponentially fast at low temperature in two-dimensional antiferromagnets, the critical temperature for three-dimensional ordering is expected to grow very fast with the inter-plane coupling, reaching quite rapidly values of the order of the intra-plane couplings. In that situation, the two transitions might very well merge into a single phase transition, with a critical behavior that could be very different from the standard one for magnetic ordering of three-dimensional Heisenberg antiferromagnets though. Given the lattice sizes available when phonons are included, this is an issue we could not address however.

From an experimental point of view, the first prototype of the spin-1/2 $J_1-J_2$ model has been recently synthesized. It is a layered vanadium oxide Li$_2$VOSiO$_4$ in which VO$_6$ pyramids are arranged in such a way that second vanadium neighbors are in the same plane while first neighbors are not, so that $J_2$ need not be smaller than $J_1$. Although there is no general agreement on the precise value of the ratio $J_2/J_1$, both experimental and theoretical estimates lead to a ratio significantly larger than 1/2. Therefore, the system is expected to develop collinear order, which has been confirmed by NMR results at the Li site. Indeed, the NMR spectrum at this site clearly shows that, below $T_c \sim 2.8K$, the central peak splits into three different peaks that correspond to different Li sites where the local field is either zero or nonzero (parallel or antiparallel to the external field). This behavior has been associated to a magnetic order where the spins lie along the $x$ direction with the magnetic vector $Q = (0, \pi)$. Moreover, the $^{29}$Si NMR spectrum is very anomalous at low temperature and given the very symmetric position of Si in the lattice, this cannot be attributed to the development of collinear order but must be related to a structural phase transition. Given the rather low characteristic temperatures in that system ($T_c \simeq 2.8K$ while the transfer of weight of the Si line is complete at 2 K), a precise structural determination of the low temperature phase has not been possible yet. Interestingly enough, the temperature at which the system starts to develop a structural distortion seems to be slightly larger than $T_c$, which would agree with the general expectation for small inter-plane coupling. Indeed, experimentally, it is not possible to exclude that distorted regions start to generate above 2.8K and grow, by decreasing the temperature, by a nucleation procedure. Whether a more direct determination of the structural transition will confirm this point remains to be seen.

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