Magnetoelastic Instability in Molecular Antiferromagnetic Rings

Leonardo Spanu[1] and Alberto Parola[2]

[1]*INFM and Dipartimento di Fisica "A. Volta," Università di Pavia, I-27100 Pavia, Italy*
[2]*INFM and Dipartimento di Fisica e Matematica, Università dell'Insubria, I-22100 Como, Italy*

(Received 4 December 2003; published 13 May 2004)

Lattice stability in a model of an antiferromagnetic ring coupled to adiabatic phonons is investigated for different values of the spin and numbers of magnetic sites. The magnetoelastic transition is shown to be heavily affected by the spin value, displaying a qualitative difference in the nature of the instability for spin one-half. Among the different synthesized materials, Cu_8 seems to be the best candidate to observe lattice dimerization in these systems. Our analysis excludes stable lattice distortions in higher spin rings. The effects of thermal fluctuations are studied in the Cu_8 model, where a characteristic crossover temperature is estimated.

DOI: 10.1103/PhysRevLett.92.197202 PACS numbers: 75.10.Pq, 65.80.+n, 81.07.Nb

Magnetic molecular rings (MMR), with nearest neighbor antiferromagnetic (AF) interactions, are ideal materials for exploring the crossover from microscopic magnetism to collective effects in low dimensional systems. Rings with a different value of the spin S and number N of magnetic sites have been synthesized in recent years [1]. They give the opportunity to understand how the static and dynamical properties of the material are affected by a change in the spin value or a change in the number of magnetic sites. Considerable attention has been devoted to the observation of resonant tunneling of the magnetization in single-molecule superparamagnets [2] and of quantum steps of magnetization in molecular AF rings [3,4].

Ring-shaped molecular clusters, such as Fe_6 [4], Fe_{10} [5], Cr_8 [6], and Cu_8 [7], have been studied by several techniques, such as nuclear magnetic resonance (NMR) [8,9], calorimetric measurements, x rays, and inelastic neutron scattering (INS). Recently, INS experiments performed on Cr_8 molecular rings [10] have been interpreted on the basis of a distorted ring geometry at low temperature, in contrast to the centrosymmetric structure suggested by x-ray diffraction at room temperature. In the Cu_8 rings, the Cu nuclear quadrupole resonance (NQR) spectrum shows four structurally nonequivalent Cu ions [9]: An open question is whether the reduced symmetry is related to the appearance of dimerization. Heat capacity and magnetic torque measurements in magnetic field may also suggest the occurrence of a dimerized phase in Fe_6:Li at $T = 1$ K [11].

The spin-Peierls (SP) transition is a magnetoelastic instability which occurs in a spin chain coupled with the lattice. It occurs when a distorted phase characterized by a lattice dimerization is stabilized below a critical temperature T_c due to the gain in magnetic energy. Such a transition was first predicted to occur in the (infinite) $S = 1/2$ Heisenberg AF chain [12] and it was indeed observed experimentally in the quasi-one-dimensional $S = 1/2$ compound $CuGeO_3$ [13]. A number of results have been obtained both analytically [14] and numerically [15] for the spin one-half Heisenberg chain coupled to the phonons. Few investigations have been performed in the case of finite rings and/or higher spin [16]. On general grounds we observe that, in the thermodynamic limit, the dimer susceptibility of the Heisenberg chain is known to diverge as $|\pi - q|^{-1}$ (with logarithmic corrections) for wave vectors close to $q = \pi$ and *arbitrary* semi-integer spin S [17], leading to SP instability at $T = 0$. The situation is different in a finite-size system or in chains with integer spin S, where the singlet gap in the excitation spectrum gives a finite susceptibility also in the $T \to 0$ limit. Therefore, we expect that in MMR the lattice distortions will be stabilized only for a sufficiently small elastic constant. The competing role of finite-size effect and of thermal fluctuations in these systems has not yet been clarified.

In this Letter, we first analyze the stability of a mesoscopic magnetic ring with respect to lattice distortions and then we examine the finite temperature effects in these systems. Surprisingly, a *qualitative* difference between the behavior of $S = 1/2$ and higher spin rings is found, strongly suggesting the absence of stable lattice distortion in the latter case. Among the synthesized MMR, Cu_8 seems to be the only candidate to display a magnetoelastic instability for realistic values of the phonon coupling. An estimate of the crossover temperature associated to this "transition" is also given.

We focus on rings with an even number of sites, in which the AF superexchange coupling leads to a singlet ground state. We investigate the simplest model Hamiltonian containing both AF interaction and spin-lattice coupling:

$$\mathcal{H} = J \sum_{j=1}^{N} [1 + \alpha \delta_j] \vec{S}_j \cdot \vec{S}_{j+1} + \frac{K}{2} \sum_{j=1}^{N} \delta_j^2, \qquad (1)$$

where K is the spring constant, δ_i is the distortion of the bond between site i and $i + 1$, α is the spin-lattice

coupling, and the last term is the elastic energy. Periodic boundary conditions are understood ($S_{N+1} = S_1$). Lattice distortions are treated in the adiabatic approximation, i.e., δ_i are c numbers. Because of the uncertainties in the modeling of the microscopic mechanisms leading to the spin-phonon coupling in these materials, harmonic approximation has been employed in the form of Hamiltonian (1), thereby limiting its validity to the $\alpha|\delta_i| \ll 1$ case. We did not include in the Hamiltonian other terms, usually present in the microscopic description of MMR [10], which do not directly couple with the lattice, such as dipolar interactions or spin anisotropies. The invariance of the Hamiltonian under the rescaling $\alpha \to \lambda\alpha$, $K \to \lambda^2 K$, and $\delta_i \to \delta_i/\lambda$ allows one to restrict the parameter space by setting $\alpha = 1$ without loss of generality. The further constraint, due to periodic boundary conditions, $\sum_i \delta_i = 0$ is also understood. By relaxing this constraint, the numerical results remain qualitatively unchanged.

The ground state of Hamiltonian (1) is obtained in two steps [18]: First, by the Lanczos technique, we determine the lowest energy eigenvalue of (1) at fixed $\{\delta_i\}$. The bond distortions are then updated in order to comply with the equilibrium condition obtained by use of the Hellman-Feynman theorem:

$$K\delta_j - J\langle \vec{S}_j \cdot \vec{S}_{j+1}\rangle_\delta - \frac{J}{N}\sum_{i=1}^{N}\langle \vec{S}_j \vec{S}_{j+1}\rangle_\delta = 0, \qquad (2)$$

where $\langle \cdots \rangle_\delta$ is the ground state expectation value, in the presence of distortion. No lattice symmetry has been assumed, in order to investigate all the possible lattice equilibrium configurations. In all cases we examined, we found either an undistorted configuration or a dimerized ring, i.e., $\delta_i = (-1)^i \delta_0$. No other periodicity has been observed, as already known for $S = 1/2$ [19].

The numerical results concerning the stability of the undistorted phase are reported in Fig. 1. The distortion amplitude is plotted as a function of the elastic constant, for different values of the spin. All models we examined show a critical constant K_c beyond which the symmetric phase is unstable. The results clearly show that, while in the spin one-half case the transition is continuous, for larger spin the distortion amplitude δ_0 suddenly jumps from zero to a finite value (even larger than the lattice spacing) when the spring constant is reduced. Although such a large distortion falls outside the range of validity of the model, the results clearly point toward a first order transition in the $S > 1/2$ case. No qualitative differences between integer and semi-integer spins can be observed in these small rings.

In order to understand the origin of the different behavior of the $S = 1/2$ case, we have performed Lanczos diagonalizations fixing the dimerization amplitude δ_0, and we computed the ground state energy of the dimerized Heisenberg model $E_H(\delta_0)$. In terms of this quantity the equilibrium condition reads

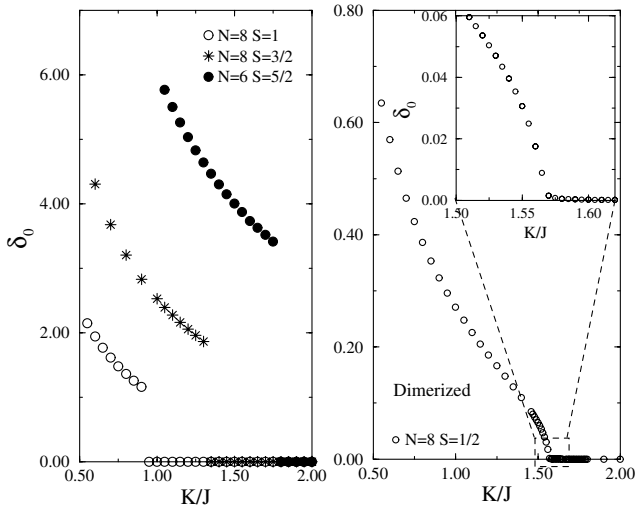

FIG. 1. Stability diagram for different sizes N and spin S, corresponding to synthesized materials. Spring constant K in units of J. Left panel: $N = 6$, $S = 5/2$ (Fe_6); $N = 8$, $S = 3/2$ (Cr_8) and $N = 8$, $S = 1$. Right panel: $N = 8$, $S = 1/2$ (Cu_8). Inset: blowup of the Cu_8 stability diagram for $K \sim K_c$.

$$\frac{d}{d\delta_0}\left[E_H(\delta_0) + \frac{N}{2}K\delta_0^2\right] = 0. \qquad (3)$$

$\delta_0 = 0$ is always a solution, $E_H(\delta_0)$ being analytic in δ_0^2. Generally, lattice distortions lower the magnetic energy E_H for any S, making the undistorted phase stable only for $K > K_c$, with

$$K_c = -\frac{1}{N}E_H''(\delta_0)\Big|_{\delta_0}, \qquad (4)$$

where the prime denotes a derivative with respect to the dimerization amplitude. The second derivative of the ground state energy (i.e., the dimer susceptibility) on the right-hand side of Eq. (4) can be evaluated numerically for several N and S. The resulting critical couplings K_c are shown in Fig. 2, suggesting an approximate linear scaling with S. Note that the natural energy scale of the problem is set by the classical magnetic term $\sim JS^2$. Therefore, the *dimensionless* critical spring constant K_c/JS^2 actually scales as $1/S$ and vanishes in the classical limit $S \to \infty$. Following the standard Landau-Ginzburg approach, the equilibrium distortion amplitude is predicted to continuously evolve from zero to finite values as K is reduced below K_c. This expectation rests on the assumption of a *positive* fourth order term in the expansion of $E_H(\delta_0)$ about $\delta_0 = 0$. We checked this condition by computing the fourth derivative of E_H at $\delta_0 = 0$ which turns out to be positive only in the $S = 1/2$ case, as shown in Table I. Therefore, for $S > 1/2$, the transition is indeed first order as suggested by the numerical results of Fig. 1. This numerical finding is confirmed by studying the $S \to \infty$ limit of our model (1). For a dimerized ring,

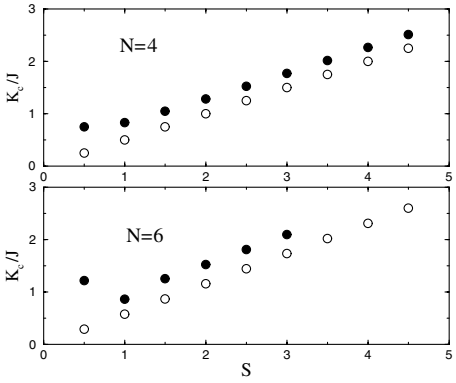

FIG. 2. Scaling relation for K_c in units of J as a function of the spin S, for $N = 4$ (top panel) and $N = 6$ (bottom panel). Black filled symbols are Lanczos data, empty symbols spin-wave results.

the classical ground state energy $E_H^{\rm cl} = -J\sum_i[1 + (-1)^{-i}\delta_0]S^2 = -NJS^2$ becomes independent of the distortion amplitude δ_0. It follows that, classically, the distortion does not decrease the magnetic energy contribution and, hence, a dimerized geometry is not favored. Only quantum fluctuations lift the degeneracy in δ_0. In order to estimate the effects of quantum fluctuations on the ground state energy, we made use of lowest order spin-wave theory (SWT) for finite-size chains [20] which is free from singularities even in 1D. By applying SWT to the dimerized Heisenberg ring, we obtain the $O(S)$ expression for $E_H(\delta_0)$:

$$E_H(\delta_0) = -NJS(S+1) + 2SJ\sqrt{1-\delta_0^2}\cot\frac{\pi}{N}, \qquad (5)$$

leading to the result

$$K_c = -\frac{1}{N}\frac{dE_H}{d\delta_0^2}\bigg|_{\delta_0=0} = \frac{2SJ\cot\frac{\pi}{N}}{N}. \qquad (6)$$

This explains the linear scaling observed in the numerical results. Direct evaluation of the fourth derivative of $E_H(\delta_0)$ from Eq. (5) confirms the first order transition in the classical limit $S \to \infty$ as shown in Table I. The continuous transition for spin one-half rings is therefore exclusively due to the enhancement of quantum fluctuations and is then a genuine quantum effect which goes beyond semiclassical treatments.

TABLE I. Fourth derivative of the ground state energy with respect to the dimerization parameter δ_0 for different sizes N and spins S. Values are divided by S. The $S = \infty$ results are obtained by use of spin wave theory [Eq. (5)].

	$S = 1/2$	$S = 1$	$S = 3/2$	$S = 2$	$S = 5/2$	$S = \infty$
$N = 4$	54.0	−18.9	−9.7	−8.2	−7.6	−6.0
$N = 6$	423.3	−72.1	−12.3	−14.7	−13.3	−10.4
$N = 8$	1589.8	−152.2	−5.5			−14.5

Some further physical insight on the difference between spin one-half and $S > 1/2$ can be gained by investigating the "proximity" between the undistorted ground state and the valence bond (VB) state, corresponding to $\delta_0 = 1$, which mimics the dimerized phase in the strong distortion limit. By calculating the overlap between these two states shown in Fig. 3, we appreciate a noticeable dependence on the spin value, the overlap getting smaller and smaller for increasing S and being significant only for $S = 1/2$. Such a decrease in the overlap suggests that a continuous transition between the undistorted and the distorted phase becomes less and less favored for spin larger than one-half at any size N.

Finally, we comment on the stability of the distorted phase against thermal fluctuations. The coupling of the spins with the lattice (considered here as embedded in the tree dimensional space) allows for a magneto-elastic transition at finite temperature, driven by the one-dimensional magnetic fluctuations. We concentrate on the behavior of $S = 1/2$ rings for only in these cases the ground state may show stable lattice distortions. In finite-size systems, no sharp transitions may be observed at finite temperature and only *crossover* temperatures can be defined. However, a sharp change at some $T_c(K)$ is expected in the distortion distributions for $K < K_c$: The low temperature bimodal distribution peaked at $\pm\delta_0$ turns into a Gaussian-like probability centered around $\delta_0 = 0$ for temperatures larger than the "mean field" critical temperature $T_c(K)$. By employing exact diagonalization in the full Hilbert space of the Hamiltonian (1), we computed the partition function and the finite temperature dimer susceptibility of the model thereby obtaining the critical temperature shown in Fig. 4. Note the steep increase in $T_c(K)$ close to the transition, implying that temperatures higher than $\sim 0.1\,J$ are always required to destabilize the lattice distortion.

Now we are ready to apply our results to real materials and discuss the possible occurrence of a dimerized phase in magnetic molecular rings. The results of Fig. 1 strongly

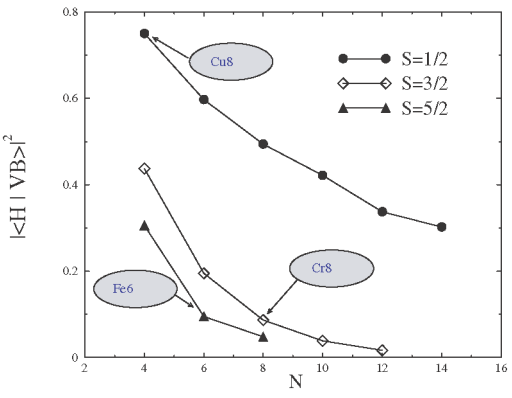

FIG. 3 (color online). Overlap between the undistorted Heisenberg ground state $|H\rangle$ and the VB state $|VB\rangle$ for different spins as a function of N.

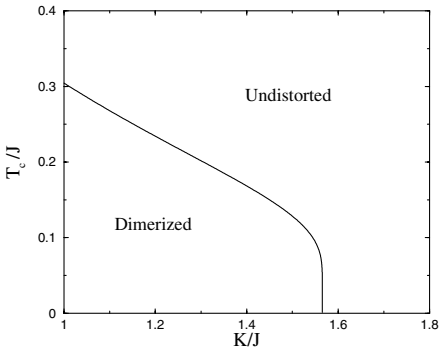

FIG. 4. Crossover temperature as a function of the elastic coupling for a $N = 8$, $S = 1/2$ MMR.

suggest that lattice distortions cannot be observed in synthesized magnetic rings with $S > 1/2$. In these cases, small distortions are never stabilized even at $T = 0$, while the occurrence of a strongly first order transition would probably disrupt the ring structure in the absence of a sufficiently hard elastic constant K. On the contrary, as show in Figs. 1 and 4, in the case of Cu_8 ($N = 8$ magnetic sites and $S = 1/2$), a stable dimerized phase is instead possible at low temperature. According to Ref. [9], the Cu_8 ring has a coupling of about $J = 0.1$ eV, the exchange interaction being due to Cu-O-Cu bridge as usual in copper-oxide compounds. Assuming a typical value for $\alpha \sim 10$, we find that small lattice distortions can be stabilized by a spring constant attaining the physically reasonable value $K \simeq 0.1 J\alpha^2 \sim 1$ eV. Instead, in iron and chromium rings the magnetic coupling is much weaker ($J \sim 1.5$ meV in Cr_8 [6,10] and $J \sim 2.4$ meV in Fe_6 [4,8]), pushing lattice instabilities to a considerably smaller value of K.

In conclusion, using SWT and Lanczos diagonalizations, we have investigated the properties of a generic AF magnetic ring, with spins adiabatically coupled to lattice distortions. We have emphasized the role of the spin in the occurrence of magnetoelastic instabilities, showing that the order of the transition strongly depends on the value of S. In order to assess the accuracy of the adiabatic approximation employed here, experimental studies on the characteristic frequencies of the phonon modes will be necessary. However, we believe that this test is not crucial for the present investigation because lattice instabilities are classical phenomena whose occurrence can be reliably estimated also in the adiabatic limit. Our analysis suggests that magnetoelastic coupling cannot be invoked for the interpretation of NMR and NQR data in MMR with spin different from one-half [11], while confirming this possibility in the case of Cu_8 [9,13]. An investigation of the effects of thermal fluctuations on the stability of the distorted phase has also been performed for the latter case. X-ray scattering at low temperature and NMR spectra analysis will be able to determine whether MMR do indeed display lattice distortions in the ground state.

L. S. thanks F. Borsa, A. Lascialfari, and Y. Furukawa for useful discussions and for showing and explaining their experimental results. We also thank F. Becca and N. Masciocchi for valuable comments. L. S. acknowledges kind hospitality at the Department of Physics of the University of Milano.

[1] D. Gatteschi, A. Caneschi, L. Pardi, and R. Sessoli, Science **265**, 1054 (1994).
[2] W. Wernsdorfer and R. Sessoli, Science **284**, 133 (1999), and reference therein.
[3] A. Chiolero and D. Loss, Phys. Rev. Lett. **80**, 169 (1998).
[4] A. Caneschi *et al.*, Chem. Eur. J. **2**, 1379 (1996); G. L. Abbati *et al.*, Inorg. Chem. **36**, 6443 (1997).
[5] K. L. Taft *et al.*, J. Am. Chem. Soc. **116**, 1055 (1994).
[6] J. van Slageren *et al.*, Chem. Eur. J. **8**, 277 (1990).
[7] G. A. Ardizzoia *et al.*, J. Chem. Soc. Chem. Commun. **15**, 1021 (1990).
[8] A. Lascialfari *et al.*, Phys. Rev. B **55**, 14 341 (1997).
[9] A. Lascialfari *et al.*, Phys. Rev. B **61**, 6839 (2000).
[10] S. Carretta *et al.*, Phys. Rev. B **67**, 094405 (2003).
[11] M. Affronte *et al.*, Phys. Rev. Lett. **88**, 167201 (2002).
[12] M. C. Cross and D. S. Fisher, Phys. Rev. B **19**, 402 (1979); M. Aizenman and B. Nachtergaele, Commun. Math. Phys. **164**, 17 (1994).
[13] M. Hase *et al.*, Phys. Rev. Lett. **70**, 3651 (1993).
[14] See, for instance, A. I. Buzdin and L. N. Bulaevskii, Sov. Phys. Usp. **23**, 7 (1980).
[15] F. Becca *et al.*, Phys. Rev. Lett. **91**, 067202 (2003).
[16] D. Guo *et al.*, Phys. Rev. B **41**, 9592 (1990); H. Onishi and S. Miyashita, Phys. Rev. B **64**, 014405 (2001).
[17] I. Affleck and F. D. M. Haldane, Phys. Rev. B **36**, 5291 (1987).
[18] A. E. Feiguin *et al.*, Phys. Rev. B **56**, 14 607 (1997).
[19] E. H. Lieb and B. Nachtergaele, Phys. Rev. B **51**, 4777 (1995).
[20] Q. F. Zhong and S. Sorella, Europhys. Lett. **21**, 629 (1993).