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Lattice effects on the spin dynamics in antiferromagnetic molecular rings

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We investigate spin dynamics in antiferromagnetic molecular rings at finite temperature in the presence of spin-phonon (*s*-*p*) interaction. We derive a general expression for the spin susceptibility in the weak *s*-*p* coupling limit and then focus on the low-frequency behavior in order to discuss a possible microscopic mechanism for nuclear relaxation in this class of magnetic materials. To lowest order in a perturbative expansion, we find that the susceptibility takes a Lorentzian profile and all spin operators (S^x, S^y, S^z) contribute to spin dynamics at wave vectors $q \neq 0$. Spin anisotropies and local *s*-*p* coupling play a key role in the proposed mechanism. Our results prove that small changes in the spatial symmetry of the ring induce qualitative changes in the spin dynamics at the nuclear frequency, providing a mechanism for nuclear relaxation. Possible experiments are proposed.

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In a crystal of molecular magnets not all physical properties and microscopic interactions can be exhaustively described by an effective Hamiltonian containing only magnetic terms. The works on magnetization tunneling in Mn_{12} compounds[1–3] clearly demonstrated that the localized spins in each molecule interact with lattice degrees of freedom, dislocations,[2–4] and organic ligand deformations,[5] changing local field at each magnetic site. Spin-lattice interactions revealed, thus, an essential ingredient for explaining the relaxation of the macroscopic magnetization in ferromagnetic clusters. In the case of antiferromagnetic (AF) rings, thermodynamic properties, such as specific heat and magnetization curves, can be rather satisfactorily described in terms of a minimal *N*-spins Hamiltonian containing only magnetic interactions

$$H_\sigma = J\sum_{j=1}^{N} \vec{S}_j \cdot \vec{S}_{j+1} + D\sum_{j=1}^{N} (S_j^z)^2 + g\mu_B \sum_{j=1}^{N} \vec{H} \cdot \vec{S}_j, \tag{1}$$

where periodic boundary conditions are understood. In addition to the dominant Heisenberg interaction and to the Zeeman coupling, the anisotropy term in Eq. (1) ($D \sim -10^{-2} J$) is an effective description of the local field at each magnetic site. This model has been also successfully adopted for interpreting the behavior of dynamical observables at the electronic-frequency–electron-paramagnetic resonance (EPR)[6] or inelastic neutron-scattering (INS) experiments.[7] However, Hamiltonian (1) proves not adequate for explaining nuclear relaxation phenomena in AF rings and a coupling with external degrees of freedom is then required. The discrete spectrum of the molecular magnet does not allow the relaxation between Zeeman-split nuclear levels because of the mismatch between the typical nuclear energy scale ($10^{-5} J$) and the electronic one (ranging from J to $g\mu_b H \sim 10^{-2} J$). NMR experiments performed on AF rings[8] suggest the relevance of the spin-phonon (*s*-*p*) coupling for understanding and explaining the relaxation rate $1/T_1$ (Refs. 8–10) and, more generally, the spin dynamics at very low frequency in these systems. In spite of the large amount of experimental NMR data available in Fe_6 (Ref. 9) and Cr_8,[10] a comprehensive microscopic description of the relaxation mechanism in AF rings at finite temperature and weak magnetic field is still missing. Past investigations were mainly focused on the dynamics at high magnetic field and zero temperature in connection to the problem of tunneling of the Néel vector.[11] Assuming that the Hamiltonian (1) is a good starting effective model for the AF rings, a central problem is to clarify which spin mechanisms control the low-frequency dynamics, allowing one to observe the Lorentzian profile of the relaxation rate $1/T_1$ and its strong frequency dependence.[8,10] Moreover, it is not fully understood which magnetic property may be investigated by the nuclear relaxation measurements because of the mismatch between the nuclear and the electronic energy scale. A microscopic description of the *s*-*p* effects on the spin dynamics should also help the identification of the decoherence mechanism in this class of materials, the interaction of the spins with external degrees of freedom strongly limiting possible future technological applications.[12]

In this paper, we investigate the dynamical spin susceptibility in the presence of a spin-phonon coupling in order to identify the possible microscopic spin mechanisms at the basis of the observed dynamics. We derive a general expression for the dynamical spin correlation functions and then focus on the very low-frequency limit, connecting our results to the problem of the nuclear relaxation in AF rings. We will show that, to lowest order in the *s*-*p* coupling, even small perturbations breaking the reflection symmetry of the molecular ring have a profound effect on the relaxation rate due to contributions coming from the dynamics of all spin operators (S^z and S^x, S^y) at wave vectors $k \neq 0$. In a recent work based on a Master Equation formalism, Santini *et al.*[13] found that in the $\omega \to 0$ limit, the spin dynamics at low temperature, in the presence of a coupling with a thermal bath, is dominated by the S^z operator at $q=0$ wave vector. As clearly shown in a related context, however, a fully microscopic approach is often essential for clarifying quantum effects in mesoscopic spin-phonon systems.[14]

Because of *s-p* coupling, although the nucleus does not directly interact with phonons,[15] the nuclear relaxation rate $1/T_1$ probes the spin dynamics of the many-body system, the relaxation rate being expressed as[16]

$$\frac{1}{T_1} \propto \sum_{\sigma\tau} \sum_{q} [A_q^{\sigma\tau} S^{\sigma\tau}(q,\omega_L) + (A_q^{\sigma\tau})^* S^{\sigma\tau}(q,-\omega_L)]. \qquad (2)$$

In Eq. (2), $A_q^{\sigma\tau}$ are geometrical coefficients and $S^{\sigma\tau}(k,\omega)$ represents the dynamical spin correlation function at the nuclear Larmor frequency $\omega_L \sim 10^{-5}\,J$. The dynamical correlations may be conveniently expressed in Lehmann representation as

$$S^{\sigma\tau}(k,\omega) = \frac{1}{NZ_T} \sum_{i,f} e^{-\beta E_i} \langle i|S_k^{\sigma}|f\rangle\langle f|S_{-k}^{\tau}|i\rangle \times \delta(E_i - E_f - \omega), \qquad (3)$$

where S_q^{σ} is a generic single spin operator ($k=2\pi n/Nn = 0,\ldots,N-1$), and $|i\rangle$ and $|f\rangle$ are the many-body exact eigenstates of the full Hamiltonian, including spin and phonon degrees of freedom, with energy E_i and E_f, respectively. The system of interest is described by the minimal model Hamiltonian

$$H = H_{\sigma} + H_P + H_{sp} \qquad (4)$$

$$H_P = \sum_q \omega_q a_q^{\dagger} a_q \qquad (5)$$

$$H_{sp} = V(\vec{S}) \frac{1}{\sqrt{N}} \sum_q \frac{1}{\sqrt{\omega_q}} (a_q + a_q^{\dagger}), \qquad (6)$$

where a_q are the Bose operators for the (three-dimensional) phonons, ω_q the phonon frequency, and $V(\vec{S})$ is a generic spin operator describing the coupling with the phonons [*s-p* coupling constant is implicitly included in the definition of the potential $V(\vec{S})$]. Assuming that the *s-p* term weakly perturbs the spin system, we express the generic state $|i\rangle$ (and $|f\rangle$) in Eq. (3) as a product of eigenstates $|\sigma\rangle|m\rangle$, $|\sigma\rangle$ describing the spins and $|m\rangle$ the phonon degrees of freedom. To lowest order in a perturbative expansion in the *s-p* coupling, we take $|\sigma\rangle$ as an exact eigenstate of the Hamiltonian (1). Then we write the eigenvalue equation for the state $|i\rangle = |\sigma\rangle|m\rangle$ and, after projecting onto the spin state $|\sigma\rangle$, we finally obtain the equation defining the phonon state $|m\rangle$:

$$E_{\sigma}|m\rangle + \sum_q \omega_q a_q^{\dagger} a_q |m\rangle + \frac{\langle\sigma|V|\sigma\rangle}{\sqrt{N}} \sum_q \frac{1}{\sqrt{\omega_q}} (a_q + a_q^{\dagger})|m\rangle = E|m\rangle. \qquad (7)$$

The exact solutions of Eq. (7) are products over q of shifted harmonic oscillator states, the shift constant α_q^{σ} depending on the form of the *s-p* coupling $V(\vec{S})$ and on the spin state: $\alpha_q^{\sigma} = \langle\sigma|V|\sigma\rangle/\sqrt{N\omega_q^3}$. Substituting the product eigenstates into the formal expression (3), we obtain

$$S^{\sigma\tau}(k,\omega) = \frac{1}{Z} \sum_{\sigma_i,\sigma_f} \sum_{n,m} e^{-\beta(E_i + \Sigma_q \omega_q n_q)} |\langle n|m\rangle|^2 \times \langle\sigma_i|S_k^{\sigma}|\sigma_f\rangle \times \langle\sigma_f|S_{-k}^{\tau}|\sigma_i\rangle \times \delta\left[\Delta E_{if} + \sum_q \omega_q (n_q - m_q) - \omega\right], \qquad (8)$$

where $|\sigma_i\rangle$ and $|\sigma_f\rangle$ identify pure spin states with energy difference ΔE_{if} and $|n\rangle$ and $|m\rangle$ are the phonon states with phonon occupation number $\{n_q\}$ and $\{m_q\}$, respectively. The key element in Eq. (8) is the overlap between the two shifted harmonic oscillator eigenstates $|\langle n|m\rangle|$, the two shifts depending on the spin states $|\sigma_i\rangle$ and $|\sigma_f\rangle$. Using an integral representation of the δ function in Eq. (8) and the explicit expression for $|\langle n|m\rangle|$,[18] we obtain

$$S^{\sigma\tau}(k,\omega) = \frac{Z_p}{Z} \sum_{\sigma_i,\sigma_f} e^{-\beta E_i} \langle\sigma_i|S_k^{\sigma}|\sigma_f\rangle \times \langle\sigma_f|S_{-k}^{\tau}|\sigma_i\rangle I_{if}(\omega), \qquad (9)$$

where Z_p is the phonon partition function and the function $I_{if}(\omega)$ is defined (see also[19])

$$I_{if}(\omega) = \int \frac{dt}{2\pi} e^{i(\Delta E_{if} - \omega)t} \times e^{-\Sigma_q (\Delta\alpha_q)^2 [i \sin \omega_q t + \coth(\beta\omega_q/2)(1 - \cos \omega_q t)]}. \qquad (10)$$

In the simple situation of a phonon spectrum of the Debye type: $\omega_q = cq$ for $\omega < \omega_D$, taking the thermodynamic limit and considering the low-temperature behavior $\beta\omega_D \to \infty$, Eq. (11) becomes

$$I_{if} = \frac{\beta}{2} \int_{-\infty}^{\infty} \frac{dy}{2\pi} e^{-i\Omega_{if} y} e^{-\gamma\Lambda[(1/2)\beta\omega_D y]} \left[\frac{\sinh \frac{\pi}{2} y}{\frac{\pi}{2} y}\right]^{-\gamma_{if}}, \qquad (11)$$

where $\Lambda(u) = \int_0^u dz[(1 - e^{iz})/z]$ and we have introduced two important quantities, the dimensionless frequency $\Omega_{if} = \frac{1}{2}\beta(\omega - \Delta E_{if})$ and the effective coupling

$$\gamma_{if} = 3\omega_D^{-3} [\langle i|V|i\rangle - \langle f|V|f\rangle]^2. \qquad (12)$$

In the weak *s-p* coupling limit, $\gamma_{if} \to 0$ and Eq. (11) reduces to

$$I_{if}(\omega) \sim \frac{\beta\gamma_{if}}{\pi^2 \gamma_{if}^2 + 4\Omega^2}. \qquad (13)$$

Finally, factorizing the partition function in terms of phonon and spin terms $Z = Z_p Z_{\sigma}$ and collecting together the previous expressions, we obtain

$$S^{\sigma\tau}(k,\omega) = \frac{1}{Z_{\sigma}} \sum_{\sigma_i,\sigma_f} \langle\sigma_i|S_k^{\sigma}|\sigma_f\rangle\langle\sigma_f|S_{-k}^{\tau}|\sigma_i\rangle \times \frac{\gamma_{if}}{\beta(\pi^2\gamma_{if}^2/\beta^2 + (\omega - \Delta E_{if})^2)} e^{-\beta E_i}. \qquad (14)$$

Equation (14), valid in the weak coupling regime, reproduces a Lorentzian profile and allows one to connect in a nonobvious way the three different energy scales present in our problem: the nuclear, the thermal, and the magnetic. Regardless of the functional form of the spin-phonon interaction $V(\vec{S})$, we first observe that when the initial spin state $|\sigma_i\rangle$ is equal to the final one $|\sigma_f\rangle$, the effective coupling γ_{if} vanishes and I_{if} reduces to a δ function at $\omega=0$. Within our formalism, the first nonzero contribution at low frequency in Eq. (14) is obtained by summing over pairs of spin states for which $\gamma_{if}\neq 0$. If the energy gap between the initial and final states is larger than the frequency scale (i.e., $\Delta E_{if}\gg\omega$), frequency dependence in Eq. (14) can be neglected, giving thus an ω-independent relaxation rate $1/T_1$. The experimental observation of a strong frequency dependence in the $1/T_1$ suggests that other channels contribute to the relaxation mechanism of the nuclear spin. Processes involving states originally belonging to the same spin multiplet are not good candidates because the energy splitting created by the presence of both anisotropy and field in a generic orientation is two or three orders of magnitude larger than the nuclear energy scale. In order to preserve a frequency dependence in Eq. (14), we are instead forced to consider transitions between pairs of quasidegenerate spin states $E_{if}\sim\omega_L$. By examining the spectrum of Hamiltonian (1), we found that degenerate states connected by reflection symmetry—with momenta q and $-q$—are the only possible candidates for describing the mechanism governing the very low-frequency dynamics at temperature $T\sim J$, within our approach. However, in order to get a nonvanishing γ_{if} via Eq. (12), the *s*-*p* coupling operator $V(\vec{S})$ must have a nonvanishing matrix element between the two states $|q\rangle$ and $|-q\rangle$, i.e., the reflection symmetry of the ring must be explicitly broken by the spin-phonon term. Starting from the Hamiltonian (1), the interaction of each single ion with the neighboring organic atoms provides the required perturbation terms. Actually, it is well established that ligand groups surrounding each magnetic site can assume different, energetically equivalent, spatial orientations (quenched disorder), lowering the symmetry of the molecule with respect to that of a perfect coplanar ring.[7] The positions of the atoms determine the strength and type of interaction of each spin with the phonons, the spin-phonon potential being described in a quite general way by the expression

$$V=\sum_{i=1,N} C_i O(\vec{S}_i). \tag{15}$$

The operators $O(\vec{S}_i)$ describe electrical quadrupole interaction,[13,17] whereas C_i is the site-dependent *s*-*p* coupling that breaks the reflection symmetry of the Hamiltonian (1). A detailed description of the functional form of the quadrupolar operators $O(\vec{S}_i)$ and a quantitative estimate of each local spin-phonon coupling is beyond the aims of our work and is not essential for a qualitative understanding of the proposed mechanism for the spin dynamics. The main point we want to stress is the existence of a site-dependent interaction, breaking the translation and reflection symmetry of the ring: the degeneracy between the two states $|q\rangle$ and $|-q\rangle$ is lifted and a nonvanishing coupling constant γ_{if} (12) is generated. The nuclear relaxation rate thus acquires a contribution from the spin dynamics at wave vector $k=2q$, showing a strong frequency dependence when the splitting created by the perturbation is comparable to the nuclear energy scale. The differences in the interactions at each magnetic site can be usually neglected at energies higher than the nuclear one, and site-dependent parameters do not improve the quality of the experimental fit.[7] On the contrary, we argue that, at the nuclear frequency, very small differences in the *s*-*p* coupling are relevant for the relaxation rate $1/T_1$. We find here a typical aspect of the disorder in correlated systems: macroscopic observables, as the $1/T_1$, are strongly affected by very small perturbations, when the perturbation itself becomes comparable to the main energy scale of the problem.

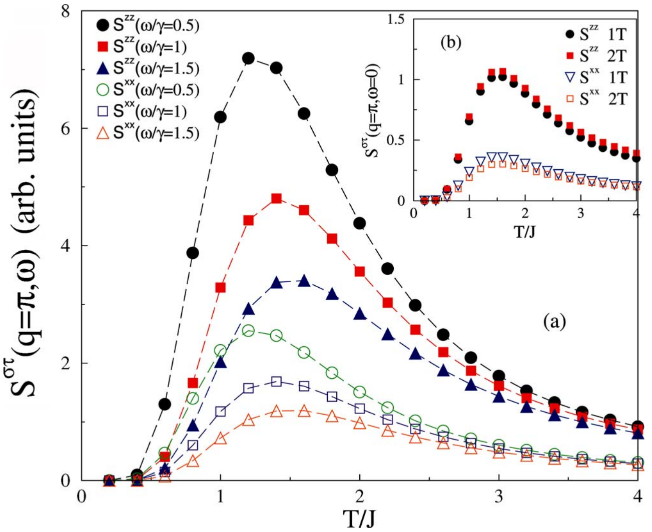

FIG. 1. (Color online) Dynamical susceptibility $S^{\alpha\beta}(q=\pi,\omega)$ as a function of the temperature T/J for Cr_8 ($N=8$; $S=3/2$; $J\sim 11.7$ K) calculated according to Eq. (14) at fixed magnetic field ($h=1$ T, $\theta=0.5$ rad) and at different frequencies (in units of J). Filled symbols refer to the S^z operator, empty to S^x. Inset: Exact Diagonalization Results for the spin susceptibility of the pure spin system (i.e., no spin-phonon coupling) at $\omega=0$, calculated at two different magnetic fields.

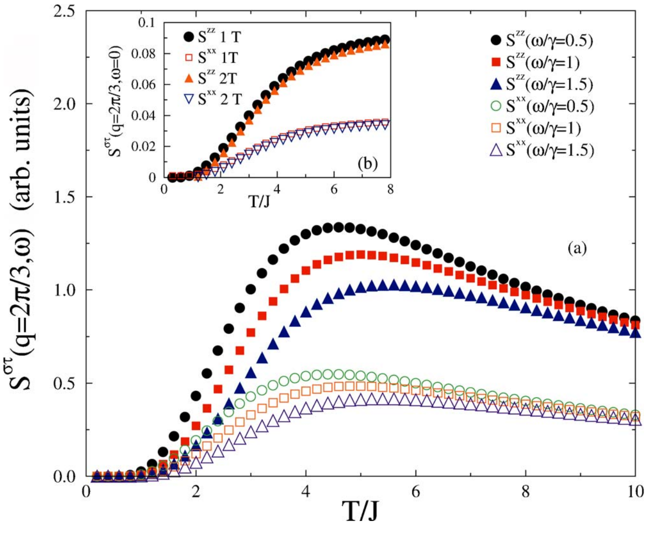

FIG. 2. (Color online) Same as Fig. 1 for Fe_6 ($N=6$; $S=5/2$; $J\sim 28$ K).

Exact diagonalizations have been performed in order to evaluate the low-frequency behavior of the dynamic correlations in Cr_8 and Fe_6 molecular rings. In Figs. 1 and 2 we report the results for the dynamical susceptibility $S^{\sigma,\tau}(k,\omega)$ as a function of temperature T/J from Eq. (14), for the Cr_8 ($k=\pi$) and Fe_6 ($k=2\pi/3$) compounds. Calculations are performed at fixed magnetic field ($h=1$ T, in the direction $\theta=0.5$ rad) and for different frequencies, including in Eq. (14) pairs of quasidegenerate states. The dynamical susceptibility of both S^z and S^x operators shows a maximum as a function of the temperature, the value of the maximum decreasing and its position moving to higher temperatures when the frequency is increased. This behavior qualitatively reproduces the experimental observations in both materials.[8] The matrix elements in Eq. (14) are only weakly dependent on the magnetic field, as can be inferred from the results for the spin susceptibility $S(k,\omega=0)$ of the pure spin Hamiltonian (insets of Figs. 1 and 2). Our results support the conclusion that the external magnetic field affects the relaxation rate mainly through the Larmor frequency $\omega_L=\Gamma_L H$.[8] In conclusion we investigated low-frequency spin dynamics at finite temperature in AF rings in the presence of *s*-*p* coupling, deriving a general expression for the dynamical susceptibility. We emphasized the central role of the lattice degrees of freedom, showing that the interaction of the spins with the surrounding atoms can generate a contribution to the dynamics at the nuclear frequency from nondiagonal operators $S^{\pm}_{2q}$, $q\neq 0$. Small changes in the spatial symmetry of the ring thus induce effects in the spin dynamics at low frequency. A characteristic feature of our expressions is that the low-frequency dynamics acquires a nonzero contribution from all spin operators S^z and $S^{\pm}$. For isotropic hyperfine coupling $A^{\sigma\tau}\propto\delta^{\sigma\tau}$ (uniform magnetic field along z direction, radio-frequency field in x direction), $1/T_1$ involves only matrix elements of $S^{\pm}$. NMR experiments performed on Cr nucleus in Cr_8 or on $^{57}\mathrm{Fe}$ in Fe_6, should provide an interesting test for detecting the contribution coming from transverse spin fluctuations at $q\neq 0$. Conversely, the proposed mechanism is excluded or strongly suppressed when the reflection symmetry is broken at an energy scale larger than the nuclear one. By applying hydrostatic pressure it is, in principle, possible to modify the global symmetry of each molecule, verifying the role of the reflection symmetry breaking on the nuclear relaxation.

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