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Magnetically driven lattice instabilities

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The spin-lattice interaction, which very recent experiments suggest is significant in the layered perovskites, is modeled by adding to the coupling constant of the anisotropic Heisenberg antiferromagnet a linear dependence on the lattice configuration. It is found that (a) the spin-lattice interaction softens the mode with wavelength of twice the lattice parameter, (b) at finite tempertures the lattice symmetry breaks and the system becomes dimerized, and (c) the dimerization vanishes exponentially as the temperature approaches $T=0$. The calculation assumes a one-dimensional model. However, the extension to higher dimensionalities is straightforward.

Apart from its obvious importance as the parent compound of a class of high-T_c superconductors, $La_2CuO_{4-\delta}$ is interesting for its remarkable magnetic properties. Experiments show that, for small enough δ, this material exhibits three-dimensional antiferromagnetic order.[1] The Néel temperature T_N may be as high as $T_N=240$ K, but decreases rapidly with the oxygen deficiency δ. However, long-ranged two-dimensional antiferromagnetic correlations in the CuO_2 planes characteristic of these layered perovskites do survive for temperatures well above T_N.[2] It is not yet clear how the two-dimensional antiferromagnetic order is affected by δ but indirect evidence has been provided on its connection with the tetragonal-to-orthorhombic structural phase transition.[3] Neutron scattering experiments on the closely related compound $La_2NiO_{4+\delta}$, also a layered perovskite, show that for $\delta\approx 0.05$ the three-dimensional antiferromagnetic order sets in at $T_N=70$ K and a tetragonal-to-orthorhombic transition takes place at $T_s=240$ K. Strong two-dimensional antiferromagnetic correlations are observed for $T_N\leq T\leq T_s$, but the correlation length is drastically reduced[3] when the temperature surpasses T_s.

Thus, it seems to be an experimental fact that in the layered transition-metal oxides the coupling between the spin and lattice degrees of freedom is not negligible.

With this motivation we studied the Heisenberg Hamiltonian with a phenomenological spin-lattice coupling. Technically, we generalize an analytical nonperturbative solution for the anisotropic antiferromagnetic Heisenberg model, which is valid for strong antiferromagnetic order, published recently.[4-6] Since the method relies on the magnetic order, it works, in principle, in the quasi-Ising asymptotic limit. However, the comparison of the results for the ground-state energy, correlation coefficients, and structure of the ground state with elaborate computer calculations shows that the analytic asymptotic solution is very accurate in an unexpectedly wide range of the anisotropy parameter[6,7] α ($\alpha=0$: Ising model; $\alpha=1$: isotropic Heisenberg model). For the linear chain the ground state is accurate to 0.5% for $0\leq\alpha\leq 0.5$.[6] For the square lattice the situation is much better, and the uncertainty for $0\leq\alpha\leq 1$ turns out to be smaller than 0.3%,[7] when compared with results of an elaborate quantum Monte Carlo simulation.[8]

Therefore, the method of solution employed below is ideal for the square lattice, since it works even for the isotropic case.[7] However, in the present stage we wish to emphasize the physical ideas, and choose to treat the one-dimensional model to gain mathematical simplicity and clarity. The extension to higher dimensionalities is immediate, and can be done applying the ideas of Ref. 7.

The results are quite striking. We found that the spin-lattice interaction induces a lattice unstability. Depending on the strength of the elastic coupling, the ground state may or may not be distorted. In the former case the harmonic approximation simply collapses at $T=0$, and the linear chain has a dimerized structure determined by the anharmonic terms. If the harmonic interaction is strong enough, the ground state involves no lattice distortion. However, as the temperature is raised from $T=0$, the system becomes progressively dimerized.

It is physically evident that the antiferromagnetic order, which has a periodicity of twice the lattice parameter, will couple predominantly with the lattice mode of the same wavelength. Thus, since we are primarily interested in qualitative trends, we can drop all the other modes and write, for the Hamiltonian of the system,

$$H=N\left(\frac{P^2}{2M}+\tfrac{1}{2}KQ^2\right)+\sum_l [J+\gamma(-1)^l Q]\{s_z(l+1)s_z(l)+\alpha[s_x(l+1)s_x(l)+s_y(l+1)s_y^{(l)}]\}\,, \tag{1}$$

where $P^2/(2M)$ is the kinetic energy of an ion, $l=1,2,\ldots,N$ characterizes the chain sites, $(-1)^l Q$ represents the ionic displacement at site l associated to a lattice wave having wavelength of twice the lattice parameter, $s_i(l)$ is the i component of the spin at site l, γ is a coupling constant, and α is the anisotropy parameter.

In the spirit of the adiabatic approximation (the spins respond rapidly to changes in the ionic configuration) we can drop $P^2/(2M)$ in a first step. The Hamiltonian then reads

$$H=\sum_l [J+\gamma(-1)^l Q]\{s_z(l+1)s_z(l)+\frac{\alpha}{2}[s_+(l+1)s_-(l)+s_+(l)s_-(l+1)]\}+\tfrac{1}{2}NKQ^2\,, \tag{2}$$

where Q plays now the role of a parameter, J is a constant, and $s_\pm = s_x \pm i s_y$.

For small enough values of α one can assume large antiferromagnetic order in the sense

$$\langle s_z(l)\rangle \approx (-1)^l \tfrac{1}{2}\,. \tag{3}$$

The Hamiltonian (2) with condition (3) for α can be diagonalized by the procedure described in detail in Refs. 4 and 5. Although these previous works deal with the anisotropic Heisenberg model with no coupling with the lattice modes ($\gamma=0$), the method of solution applies equally well to our present problem. The extension to more than one dimension can be accomplished quite straightforwardly. However, for the increase of the range of α in which the theory is valid ($0\le\alpha\le 0.5$ and $0\le\alpha\le 1$, for one[6] and two[7] dimensions, respectively) the dimensionality seems to determine no major difference.

In order to deal with the system at finite temperatures we introduce here new excitations, which were not considered in Refs. 4 and 5. Although they do not contribute to the ground state, they are important for the spectrum. We define the operators

$$\phi_e^\dagger(k)=\left(\frac{2}{N}\right)^{1/2}\sum_{l=\text{even}} e^{ikl}s_+(l+1)s_-(l)+\alpha\left(\frac{N}{8}\right)^{1/2}\frac{J+\gamma Q}{J-\gamma Q}\delta_{k,0} \tag{4}$$

and

$$\phi_o^\dagger(k)=\left(\frac{2}{N}\right)^{1/2}\sum_{l=\text{odd}} e^{ikl}s_+(l)s_-(l+1)+\alpha\left(\frac{N}{8}\right)^{1/2}\frac{J-\gamma Q}{J+\gamma Q}\delta_{k,0}\,, \tag{5}$$

which for $\gamma=k=0$ reduce to the ones defined previously.[4,5] In Eqs. (4) and (5) k is in the Brillouin zone of one of the two sublattices determined by the antiferromagnetic spin alignment. In the asymptotic regime of high antiferromagnetic order the commutation relations satisfied by the ϕ operators tend to[4,5]

$$[\phi_e(k),\phi_e^\dagger(k')]=[\phi_o(k),\phi_o^\dagger(k')]=\delta_{k,k'}\,, \tag{6}$$

$$[\phi_e(k),\phi_o(k')]=[\phi_e(k),\phi_o^\dagger(k')]=0\,, \tag{7}$$

and

$$\left[\sum_l [J+\gamma(-1)^l Q]s_z(l+1)s_z(l),\phi_e^\dagger(k)\right]=(J-\gamma Q)\left[\phi_e^\dagger(k)-\alpha\left(\frac{N}{8}\right)^{1/2}\frac{J+\gamma Q}{J-\gamma Q}\delta_{k,0}\right], \tag{8}$$

$$\left[\sum_l [J+\gamma(-1)^l Q]s_z(l+1)s_z(l),\phi_o^\dagger(k)\right]=(J+\gamma Q)\left[\phi_o^\dagger(k)-\alpha\left(\frac{N}{8}\right)^{1/2}\frac{J-\gamma Q}{J+\gamma Q}\delta_{k,0}\right]. \tag{9}$$

Combining Eq. (2) with the definitions (4) and (5) the Hamiltonian (2) becomes

$$H=\sum_l [J+(-1)^l\gamma Q]s_z(l+1)s_z(l)+\frac{\alpha}{2}(J+\gamma Q)\frac{N}{2}[\phi_e^\dagger(0)+\phi_e(0)]+\frac{\alpha}{2}(J-\gamma Q)\frac{N}{2}[\phi_e^\dagger(0)+\phi_e(0)]$$
$$-N\frac{\alpha^2}{4}\left[\frac{(J+\gamma Q)^2}{J-\gamma Q}+\frac{(J-\gamma Q)^2}{J+\gamma Q}\right]+\tfrac{1}{2}NKQ^2\,. \tag{10}$$

Equations (6)-(10) yield

$$[H,\phi_e^\dagger(k)]=(J-\gamma Q)\phi_e^\dagger(k)\,, \tag{11}$$

$$[H,\phi_o^\dagger(k)]=(J+\gamma Q)\phi_o^\dagger(k)\,. \tag{12}$$

Hence

$$H=\sum_k[(J-\gamma Q)\phi_e^\dagger(k)\phi_e(k)+(J+\gamma Q)\phi_o^\dagger(k)\phi_o(k)]+E_0(Q)\,, \tag{13}$$

where $E_0(Q)$ is the ground-state energy.

The ground state $|g(Q)\rangle$ is determined by the set of equations

$$\phi_e(k)|g(Q)\rangle=\phi_o(k)|g(Q)\rangle=0\,, \tag{14}$$

whose solution is[4,5]

$$|g(Q)\rangle=\exp\left[-\frac{\alpha}{2}\left(\frac{N}{2}\right)^{1/2}\frac{J+\gamma Q}{J-\gamma Q}[\phi_e^\dagger(0)-\phi_e(0)]-\frac{\alpha}{2}\left(\frac{N}{2}\right)^{1/2}\frac{J-\gamma Q}{J+\gamma Q}[\phi_o^\dagger(0)-\phi_o(0)]\right]|\mathcal{N}\rangle\,, \tag{15}$$

where $|\mathcal{N}\rangle$ is the Néel state which assigns the spins up to the sites of even l.

The ground-state energy $E_0(Q)$ is obtained from inserting the *ket* (15) and the original expression (2) of H in the eigenvalue equation $H|g(Q)\rangle = E_0(Q)|g(Q)\rangle$, and using the commutation properties (6)–(10) to isolate $E_0(Q)$. We found[4,5]

$$\frac{E_0(Q)}{N} = -\frac{\alpha^2}{8}\left[\frac{(J-\gamma Q)^2}{J+\gamma Q}+\frac{(J+\gamma Q)^2}{J-\gamma Q}\right] - \tfrac{1}{4}J+\tfrac{1}{2}NKQ^2, \quad J>\gamma Q. \tag{16}$$

Thus, the contribution of the spin-lattice coupling to the ground-state energy has a maximum at $Q=0$. Retaining terms only up to second order in Q one is left with

$$\frac{E_0(Q)}{N} = -\tfrac{1}{4}(1+\alpha^2)J+\tfrac{1}{2}\left[K-2\frac{\alpha^2\gamma^2}{J}\right]Q^2. \tag{17}$$

Hence, the spin-lattice interaction softens the lattice mode having wavelength of twice the interatomic distance.

It is apparent from Eq. (17) that the ground state is unstable in the extreme case when $K<2\alpha^2\gamma^2/J$. The harmonic approximation then breaks down and anharmonic terms have to be taken into account in order to stabilize the lattice. The new lattice configuration then have a dimerized structure.

Let us concentrate now in the more likely situation in which the elastic energy is larger than the magnetic energy gained from dimerizing the system ($K>2\alpha^2\gamma^2/J$). Then the ground state is not distorted. However, it will be shown in the next paragraphs that the system is driven continuously to a dimerized structure as the temperature is raised from $T=0$. One may think of this interesting property of the model as a sort of Jahn-Teller effect of magnetic origin.

The energy of an excited state of the Hamiltonian (2) reads

$$\frac{E(Q)}{N} = -\tfrac{1}{4}(1+\alpha^2)J+\tfrac{1}{2}\left[K-2\frac{\alpha^2\gamma^2}{J}\right]Q^2 + \frac{J}{N}\sum_k [n_e(k)+n_0(k)] - \frac{\gamma}{N}Q\sum_k [n_e(k)-n_o(k)], \tag{18}$$

where $n_e(k)$ and $n_o(k)$ are the occupation numbers of the bosonic excitations (4) and (5). The Q-dependent terms in the right-hand side of Eq. (18) are the adiabatic potential governing the motion of the ions. One has for the lattice dynamics the adiabatic Hamiltonian

$$\frac{1}{N}H_{\text{latt}} = \frac{P^2}{2M}+\frac{1}{2}\left[K-2\frac{\alpha^2\gamma^2}{J}\right]Q^2 - \frac{\gamma}{N}\sum_k [n_e(k)-n_o(k)]Q, \tag{19}$$

which represents a distorted harmonic oscillator. It can be rewritten as

$$\frac{1}{N}H_{\text{latt}} = \frac{P^2}{2M}+\frac{1}{2}\left[K-2\frac{\alpha^2\gamma^2}{J}\right](Q-\delta Q)^2 - \frac{1}{2}\left[K-2\frac{\alpha^2\gamma^2}{J}\right](\delta Q)^2, \tag{20}$$

where the lattice distortion is given by

$$\delta Q = \frac{\gamma}{K-2\alpha^2\gamma^2/J}\frac{1}{N}\sum_k [n_e(k)-n_o(k)]. \tag{21}$$

The energy spectrum of H_{latt} is quite obvious and has two contributions: a purely vibrational part and the dimerization energy. In order to retain only what is essential we disregard the vibrational energy. The total energy eigenvalues then become

$$\frac{E}{N} = -\tfrac{1}{4}(1+\alpha^2)J+\frac{J}{N}\sum_k [n_e(k)+n_o(k)] - \tfrac{1}{2}\left[K-2\frac{\alpha^2\gamma^2}{J}\right](\delta Q)^2, \tag{22}$$

where δQ is related with the quantum numbers $n_e(k)$ and $n_o(k)$ through Eq. (21).

The free energy of the system is

$$\frac{1}{N}F(\delta Q,T) = k_BT\ln(1-e^{-\beta J}) - \tfrac{1}{2}\left[K-2\frac{\alpha^2\gamma^2}{J}\right](\delta Q)^2+\lambda\delta Q, \tag{23}$$

where $\beta\equiv 1/(k_BT)$, and λ is a Lagrange multiplier introduced to take into account the dependence of δQ on the quantum numbers $n_e(k)$ and $n_o(k)$, which was omitted when performing the summations yielding Eq. (23). Minimization of F with respect to δQ and T gives

$$\lambda = \left[K-\frac{\alpha^2\gamma^2}{J}\right]\delta Q \tag{24}$$

and

$$\frac{\partial\lambda}{\partial T}\delta Q = -\frac{\partial}{\partial T}[k_BT\ln(1-e^{-\beta J})]. \tag{25}$$

Combining Eqs. (24) and (25), and recalling that $\delta Q=0$ for $T=0$, one finally obtains the temperature dependence of the dimerization energy

$$E_{\text{dim}}(T)\equiv\tfrac{1}{2}\left[K-\frac{\alpha^2\gamma^2}{J}\right][\delta Q(T)]^2, \tag{26}$$

which turns out to be

$$E_{\text{dim}}(T) = -\tfrac{1}{2}k_BT\ln\left[1-\exp\left(-\frac{J}{k_BT}\right)\right]. \tag{27}$$

Therefore, as T approaches zero the dimerization energy vanishes exponentially according to the asymptotic law

$$E_{\text{dim}}(T) = \tfrac{1}{2}k_BT\exp\left(-\frac{J}{k_BT}\right), \quad T\ll\frac{J}{k_B}. \tag{28}$$

In the high-temperature range ($T\gg J/k_B$) E_{dim} grows

like $T\ln T$. However, the validity of our result (27) for $T > J/k_B$ is questionable because of the risk of violating the assumption of small displacements, which is implicit from the start.

The approximate method used to diagonalize the anisotropic Heisenberg Hamiltonian with coupling coefficient depending on the lattice configuration can be extended quite straightforwardly to higher dimensionalities. Essentially, all one has to do is to separate the lattice into two sublattices, which play the roles of the even and odd sites in the linear chain. Nevertheless, no new qualitative trend is expected to occur in two and three dimensions. Of course, two- and three-dimensional lattices are richer in competing distortion possibilities. The discussion of them, however, is out of the scope of this work and will be treated in full in a future communication.

The results obtained above may have quite interesting consequences. For example, (a) the spin-lattice coupling, though weak, tends to stabilize one of the two degenerate antiferromagnetic spin configurations and (b) since affects the lattice periodicity, the spin-lattice interaction opens temperature-dependent gaps in the electronic bands. Thus, it provides a mechanism for metal-to-insulator transition in one-dimensional systems. A material having a metallic low-temperature regime may turn into a semiconductor at higher temperatures.

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