Peierls-like transition induced by frustration in a two-dimensional antiferromagnet

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(March 22, 2022)

We show that the introduction of frustration into the spin-1/2 two-dimensional (2D) antiferromagnetic Heisenberg model on a square lattice via a next-nearest neighbor exchange interaction can lead to a Peierls-like transition, from a tetragonal to an orthorhombic phase, when the spins are coupled to adiabatic phonons. The two different orthorhombic ground states define an Ising order parameter, which is expected to lead to a finite temperature transition. Implications for Li$_2$VOSiO$_4$, the first realization of that model, will be discussed.

75.10.Jm, 71.27.+a, 74.20.Mn

Peierls transition \[1\] is well documented for quasi-one dimensional systems when the coupling to the lattice is taken into account, both for metals and for magnetic insulators. \[2\] It corresponds to a breaking of the translational symmetry, with a dimerization and a doubling of the unit cell in the case of spin chains. In strictly one-dimensional systems, the transition occurs for an infinitesimal coupling of the lattice because the gain of electronic or magnetic energy always overcomes the loss in elastic energy. For instance, for S=1/2 chains, the gain in the magnetic energy by making a lattice distortion \(\Delta E_{\text{mag}} \sim \delta^{1/3}\), whereas the loss due to elastic energy is \(\Delta E_{\text{elastic}} \sim \delta^2\), and therefore a small but finite lattice displacement is always stabilized in the thermodynamic limit. \[3\] This result is very specific to one-dimension though, and in higher dimensions structural transitions are not expected for generic spin models unless other degrees of freedom play a role, like orbital degeneracy in the cooperative Jahn-Teller effect. \[4\]

In this Letter, we present strong evidence that, when frustration is present, 2D systems can behave in a very similar way, i.e., they can undergo a lattice instability that breaks the symmetry even for very small spin-lattice coupling. Motivated by recent results obtained on Li$_2$VOSiO$_4$ \[5,6\] (see the discussion below), we concentrate on the so-called \(J_1-J_2\) model on a square lattice, where \(J_1\) and \(J_2\) stand for nearest and next-nearest neighbor antiferromagnetic exchange integrals. In this model, by increasing the frustration, there is a phase transition from Néel order to a spin-liquid phase for \(J_2/J_1 \simeq 0.38\). \[7\] The nature of the disordered phase is still under debate, and many different possibilities have been proposed. \[8\] \[11\] By increasing further the frustration \((J_2/J_1 \gtrsim 0.55)\), the ordering by disorder mechanism \[12\] is expected to stabilize a collinear order, with spins ferromagnetically aligned either along the \(x\) or the \(y\) axis and antiferromagnetically aligned along the other, corresponding to pitch vectors \(Q = (0, \pi)\) and \(Q = (\pi, 0)\), respectively. In the pure spin model, Chandra and collaborators \[13\] argued that this residual two-fold degeneracy of the ground state (GS) generates a finite-temperature, Ising-like phase transition.

However, like in the Jahn-Teller effect, where the orbital degeneracy is lifted by the electron-vibron interaction, this degeneracy might \textit{a priori} also be lifted by a structural distortion if the system is coupled to the lattice. As we shall see, this is indeed the case, and ferromagnetic and antiferromagnetic bonds acquire different lengths. In that case, it is not the translational symmetry that is broken, like in the standard Peierls transition, but the rotational symmetry. Still the analogy is very suggestive: Here, the equivalent of the two dimerized structures of the chain are two orthorhombic phases with the longer bond along the \(x\) and \(y\) directions respectively, and we will talk about a Peierls-like transition. Note that this mechanism is significantly different from the one generated by thermal fluctuations \[13\]. In particular, a structural distortion will have specific consequences for NMR, which might have already been observed in Li$_2$VOSiO$_4$. \[8\]

The \(J_1-J_2\) model coupled to adiabatic phonons is defined by the Hamiltonian:

\[
H = \sum_{\langle n.n. \rangle} \left\{ J_1 (d_{ij}) S_i \cdot S_j + \frac{K_1}{2} \left( \frac{\|\delta r_i - \delta r_j\|}{d_{ij}} \right)^2 \right\} + \sum_{\langle n.n.n. \rangle} \left\{ J_2 (d_{ij}) S_i \cdot S_j + \frac{K_2}{2} \left( \frac{\|\delta r_i - \delta r_j\|}{d_{ij}^0} \right)^2 \right\}, \tag{1}
\]

where \(S_i = (S_i^x, S_i^y, S_i^z)\) is the spin-1/2 operator at site \(i\), \(\delta r_i\) is the displacement of atom \(i\), assumed to be in the plane, and \(d_{ij}\) is the distance between atoms \(i\) and \(j\). This model depends on the following parameters: \(i\) The bare values of the positions of the atoms \(R_0^0\), which form a square lattice; \(ii\) The bare values of the exchange integrals \(J_1\) and \(J_2\), corresponding to the values of \(J_1(d)\) and \(J_2(d)\) for the bare values of the distances \(d_{ij}^0 = ||R_0^0 - R_0^0||\); \(iii\) The elastic coupling constants \(K_1\) and \(K_2\). Since these coupling constants are effective parameters - a detailed description of the lattice dynamics would involve elastic terms between transition metal atoms and ligands - we have chosen the form of Eq. \(1\), but the results are essentially the same with and elastic term proportional to \((d_{ij} - d_{ij}^0)^2/(d_{ij}^0)^2\); \(iv\) The spin-lattice coupling con-
stains $\alpha_1$ and $\alpha_2$: In transition metal compounds, superexchange theory combined with empirical dependences of hopping integrals on distance [14] leads to exchange integrals that vary like the inverse of the distance to a certain power $\alpha$, with $\alpha$ in the range $6-14$, and for small displacements we can write:

$$J_{1,2}(d_{ij}) = J_{1,2} \left( \frac{d_{ij}}{\bar{d}_{ij}} \right)^{\alpha_1,2} \approx J_{1,2} \left( 1 - \alpha_1,2 \frac{\delta d_{ij}}{\bar{d}_{ij}} \right),$$

(2)

with $\delta d_{ij} = d_{ij} - \bar{d}_{ij} \sim (\mathbf{R}_i^0 - \mathbf{R}_j^0) \cdot (\delta \mathbf{r}_i - \delta \mathbf{r}_j)/\bar{d}_{ij}$. Notice that the Hamiltonian is invariant under the rescaling $\alpha_1,2 \rightarrow \lambda \alpha_1,2$, $K_{1,2} \rightarrow \lambda^2 K_{1,2}$ and $\delta \mathbf{r}_i \rightarrow \delta \mathbf{r}_i/\lambda$. This allows one to fix one parameter among $\alpha_1$, $\alpha_2$, $K_1$ and $K_2$. The physical values of the magnetic couplings are unaffected by this transformation.

To find the optimal configuration of the bond lengths for a given value of the coupling parameters ($\alpha_1$, $\alpha_2$, $K_1$ and $K_2$) in the subspace of $S_{tot}^2 = 0$, we start from a random configuration of the site displacements and we iteratively improve the total energy by changing the lattice parameters $\delta d_{ij}$. For clarity, the exchange coupling constants at equilibrium will be denoted with tilde, e.g. $\tilde{J}_1$ and $\tilde{J}_2$, with possibly more than two of them as we shall see. This self-consistent Lanczos (SCL) technique has been successfully used for different 1D and quasi-1D models. [15] By working with the relative distances $\Delta_{ij} = \delta \mathbf{r}_i - \delta \mathbf{r}_j$, we are able to describe all kinds of structural displacements, including expansion and contraction of the lattice.

Since for a random configuration all symmetries are lost, one is limited to rather small clusters. We have performed systematic calculations for the $45^\circ$ degree tilted 8-site cluster and for the $4 \times 4$ cluster, and we have checked a number of conclusions on the 32-site cluster. It turns out that the 8-site cluster is pathological for $J_2/J_1 > 0.5$, the nearest neighbor spin-spin correlations being exactly zero. This peculiarity introduces a very strong dependence on the actual values of the spin-phonon coupling, which is definitely an artifact of this lattice size. In this regard, since for the $4 \times 4$ cluster the short-range correlations are finite for all finite values of $J_2/J_1$, this cluster is expected to give more reliable insight into the actual lattice deformations.

In Fig. 1 we show the phase diagram obtained with the SCL method for the $4 \times 4$ cluster in the case of $\alpha_2 = \alpha_1$, $K_1/J_1 = 10$, and $K_2 = 0$. This choice of $K_2 = 0$ was physically motivated by the fact that elastic constants usually decrease very fast with distance. However we have also determined the phase diagram for $K_2/J_1 = 10$. A detailed account of the dependence of the results on the precise value of $K_2$ and $\alpha_2$ will be given elsewhere, [16] but the general conclusion is that modifications are not qualitative but only quantitative, and quite small. Besides, thanks to the invariance of the Hamiltonian on the rescaling mentioned above, the phase diagram is actually the same for any ratio $K_1/J_1$ up to a rescaling of $\alpha_1$. So, although there are a lot of parameters in the model, the results discussed below are generic.

Among all the possible lattice deformations, only three are stable, depending on the values of the parameters: i) the tetragonal lattice (TL), with all the bond length equal, with only one value of $\tilde{J}_1$ and $\tilde{J}_2$. The TL preserves all the translational and rotational symmetries, and the effect of the spin-phonon coupling is only to renormalize the bond length: the GS on any finite lattice system is $\Delta d = 0$. ii) the orthorhombic lattice (OL), with two different bond lengths in the $x$ and $y$ directions, inducing two different n.n. exchange integrals $J_{xy}^\delta$ and $J_{xy}^\theta$, but only one n.n.n. exchange integral $J_3$. This phase breaks the $\pi/2$ rotational symmetry and therefore the GS is two-fold degenerate. iii) the dimerized lattice (DL), with three...
different bond lengths, breaking the translational symmetry of one lattice spacing in one direction, leading to two n.n. exchange integrals in one direction, e.g., $J_{1}^{x}$ and $J_{1}^{y}$, one in the other, $J_{1}^{z}$, and two different n.n.n. exchange integrals $J_{2}$ and $J_{2}'$. The DL breaks both the $\pi/2$-rotation and the translational symmetry along one axis, and the GS is four-fold degenerate. In Fig. 2, we show the behavior of the equilibrium exchange integrals for three different ratios of $J_{2}/J_{1}$.

![Equilibrium exchange integrals $J_{1}$ (left panels) and $J_{2}$ (right panels) as a function of the spin-phonon coupling for three different values of the ratio $J_{2}/J_{1}$ of the bare exchange integrals. The parameters are those of Fig. 1.](image)

The comparison between the 8-site and the $4 \times 4$ lattice for $J_{2}/J_{1} < 0.5$ shows that the phase-boundaries are comparable, and that both the OL and the DL regions expand from 8 to 16 sites. This gives some confidence that these phases exist in the thermodynamic limit. As we shall see, this is confirmed for the OL by LSW. The fate of the dimerized phase upon increasing the system size is difficult to assess. If the $J_{1} - J_{3}$ model without phonons has a magnetically dimerized GS in the gapped phase ($0.38 \lesssim J_{2}/J_{1} \lesssim 0.55$) as several authors have suggested, one would expect this phase to expand down to zero spin-phonon coupling around $J_{2}/J_{1} = 0.5$. The results for 8 and 16 sites do not give any indication of such a behavior, and larger system sizes would be necessary to reach a definite conclusion. Unfortunately, because of the huge amount of time needed to diagonalize larger clusters with free bond lengths, it is impossible at present to perform a systematic size scaling within the SCL approach.

To get further insight into the transition between TL and OL, we consider a similar self-consistent approach based on the spin-wave (SCSW) approximation of the Hamiltonian Eq. (1). This approximation, based on the assumption of an underlying ordered phase, is not suitable to study the DL, which is expected to be a gapped phase. Within the SCSW approximation, we allow the lattice to vary the bond lengths independently along the two spatial directions, but preserving all the translational symmetries, which only allows to describe OL and TL: $J_{2}^{x,y}(\delta) = J_{1}(1 + \alpha \delta_{x,y})$ and $J_{2}(\delta) = J_{2}[1 + \alpha \delta_{\pi} + \delta_{\gamma}/2]$ (here we only consider the case of $\alpha = \alpha_{1}$ for simplicity). The first step is to find the classical state. The two local minima are the Néel and the collinear state (whereas incommensurate phases are not stabilized), with energies per site given by

$\tilde{\epsilon}_{\alpha}^{N}(\delta) = -[J_{1}^{x}(\delta) + J_{1}^{y}(\delta)]/4 + J_{2}(\delta)/2 + K_{1}(\delta_{x}^{2} + \delta_{y}^{2})/2$ and

$\tilde{\epsilon}_{\alpha}^{C}(\delta) = [\pm J_{1}^{x}(\delta) + J_{1}^{y}(\delta)]/4 - J_{2}(\delta)/2 + K_{1}(\delta_{x}^{2} + \delta_{y}^{2})/2$, respectively. In both cases the magnetic gain is proportional to the lattice distortion. The stable configuration is obtained by minimizing with respect to $\delta_{x}$ and $\delta_{y}$. For the collinear state we find that the minimal configuration is obtained for $\delta_{x}$ different from $\delta_{y}$, $\delta_{x} = \alpha_{1}(J_{2} - J_{1})/(4K_{1})$ and $\delta_{y} = \alpha_{1}(J_{2} + J_{1})/(4K_{1})$, and its energy per site is $\tilde{\epsilon}_{\alpha}^{C} = -J_{2}/(2 - \alpha_{1}^{2}(J_{1}^{2} + J_{2}^{2}))/16K_{1})$. On the contrary, for the Néel state the configuration with $\delta_{x} = \delta_{y} = \alpha_{1}(J_{1} - J_{2})/(4K_{1})$ is stabilized, with $\tilde{\epsilon}_{\alpha}^{N} = -(J_{1} - J_{2})/2 - \alpha_{1}^{2}(J_{1}^{2} - J_{2}^{2})/16K_{1})$. Therefore, the transition from the Néel to the collinear state occurs for $J_{2}/J_{1} = 0.5$ an infinitesimal coupling with the lattice stabilizes the collinear phase, inducing a structural transition to an orthorhombic phase. On the contrary, for $J_{2}/J_{1} > 0.5$ an infinitesimal coupling with the lattice stabilizes the collinear phase. The fact that the transition line bends towards smaller values of $J_{2}/J_{1}$ (see Fig. 3) is just a consequence of the fact that $J_{2}/J_{1} > J_{2}/J_{1}$.

The presence of the structural transitions are preserved upon introducing quantum fluctuations at the LSW level, although the equilibrium distances are slightly changed from the ones found in the classical limit. The only qualitative difference is that quantum fluctuations may destroy the magnetization near the classical transition, leading to a spin-liquid state. The boundaries of this gapped phase are obtained by calculating the magnetization within LSW approximation for the equilibrium exchange integrals. Rather interestingly, by increasing the spin-phonon coupling, the disordered region shrinks, eventually leaving the possibility of a direct transition between Néel and collinear phases. The results of the SCSW calculation are shown in Fig. 3.

Outside the spin-liquid region, there is a good quantitative agreement between the SCL and the SCSW calculations in describing the TL to OL transition for small to intermediate frustration, whereas there is a difference for large frustration, i.e., $J_{2}/J_{1} \gtrsim 0.5$. Indeed, within the SCL method on the $4 \times 4$ cluster, the TL structure is always stable for small spin-phonon coupling, and this is probably an artifact of the small cluster considered. By contrast, within the SCSW method, in the collinear phase, the lattice is unstable toward an orthorhombic de-
formation for an infinitesimal spin-phonon coupling. This is expected to be definitely the real situation, because of the collinear spin arrangement, where the different magnetic correlations along the \( x \) and \( y \) directions naturally induces an instability in the underlying lattice structure.

![Energy vs lattice distortion](image)

**FIG. 3.** Energy vs lattice distortion \( \delta \) within the SCSW approximation for \( K_1/J_1 = 10, K_2 = 0, \alpha_1 = 0.1, J_2/J_1 = 0.2 \) (a) and \( J_2/J_1 = 0.6 \) (b): The case of \( \delta_x = \delta_y = \delta \) (continuous lines) and \( \delta_x = 0, \delta_y = \delta \) (dashed lines) are shown. (c): Phase diagram within the SCSW approximation for \( K_1/J_1 = 10 \). Stars indicate the points where the magnetization vanishes and lines are guides to the eye. The dashed line indicates the classical transition between the Néel state and the collinear state. In each region a sketch of the lattice is depicted.

From an experimental point of view, the first prototype of the spin-1/2 2D \( J_1-J_2 \) model has been recently synthesized. It is a layered vanadium oxide \( \text{Li}_2\text{VOSiO}_4 \) in which \( \text{VO}_3 \) 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 \( J_1 \). There is no general agreement on the precise value of the ratio \( J_2/J_1 \), but both experimental and theoretical estimates lead to a ratio significantly larger than 1/2: NMR, muon spin rotation, magnetization and specific-heat measurements suggest that \( J_2/J_1 \approx 1.1 \) with \( J_1 + J_2 \approx 8K \), while and LDA calculation by Rosner et al. found that \( J_2/J_1 \) is of the order 10. In any case, the system is expected to develop collinear order, which has been confirmed by NMR results at the Li site. Interestingly enough, the \( ^{29}\text{Si} \) 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 \( (T_c \approx 2.8K) \) 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. On the basis of the results of the present work, we would like to propose that this is related to the natural instability of the collinear phase toward an orthorhombic distortion that we have identified in the \( J_1-J_2 \) model coupled to the lattice.

In summary, we have shown that frustration can lead to a Peierls-like transition when the coupling to the lattice is taken into account. This has been proven for the \( J_1-J_2 \) model, which is expected to have a zero-temperature spontaneous instability towards an orthorhombic phase for infinitesimal spin-lattice coupling when the collinear order take place. This effect, which is related to the presence of a residual degeneracy of the GS after quantum fluctuations have been taken into account, is expected to be efficient in other quantum frustrated antiferromagnets, and work is in progress along these lines. For the \( J_1-J_2 \) model, another surprise came from the parameter range in which a dimerized phase is stabilized. This phase seems to be limited to large values of the spin-lattice constant, while it is also expected to occur for infinitesimal coupling if dimer order is present in the gapped phase around \( J_2/J_1 = 0.5 \). It would be very exciting to have a physical realization of the \( J_1-J_2 \) model in that parameter range to have an experimental input regarding the relevance of that phase.

We would like to thank P. Carretta, S. Miyahara, D. Poilblanc, and L. Capriotti for many useful discussions and the Swiss National Fund.

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