Modulated Phases in Spin-Peierls Systems

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Summary: Lattice modulations in the high magnetic field phase and close to impurities in spin-Peierls systems are considered and compared to experiment. Necessary extensions of existing theories are proposed. The influence of zero-point fluctuations on magnetic amplitudes is shown.

The discovery of the first inorganic spin-Peierls substance CuGeO$_3$ by Hase et al. [1] renewed the interest in the phases of spin-Peierls substances (for reviews, see [2]). The constituting element of these substances are quasi one-dimensional spin chains coupled to the lattice degrees of freedom. The incommensurably modulated (I) phase is particularly interesting since this phase is the most complex one from the theoretical and from the experimental point of view. Already 20 years ago much work was devoted to it (e.g. [3-9]). Yet, detailed experimental investigations of the nature of this phase were not possible at that time. This has changed for CuGeO$_3$.

X-ray experiments in the I phase permitted to detect the incommensurability of the lattice in $k$-space [10]. The structure of the lattice modulation was investigated by measuring the intensity of the third harmonic [10]. The distribution of local magnetizations in CuGeO$_3$ was measured by NMR [11]. Recently, the shape and the amplitude of the magnetic part of a soliton were deduced [11, 12].

Here we will review several aspects of the theoretical description of the I phase. Special emphasis is put on the discrepancies between the so far existing theories and the experimental findings and to resolving these discrepancies [13].

The term “soliton” will be used for the combination of a zero in the modulated distortion and the concomitant localized spinon [4, 14]. The distortive soliton width $\xi_d$ is the width of the kink-like modulation. The magnetic soliton width $\xi_m$ is the spatial width of the local magnetizations [4, 13, 14]. The incommensurate modulation in the I phase is viewed as an equidistant array (lattice) of solitons.

The schematic phase diagram in Fig. 1 shall serve as a guide for the following discussion. For the sake of concreteness we consider the Hamiltonian

$$H = \sum_i J [(1 + \delta_i)S_{i+1}S_i + \alpha S_{i+1}S_{i-1}] + \frac{K}{2} \delta_i^2$$  \hspace{1cm} (0.1)

which neglects the phonon dynamics (adiabatic treatment) since the distortions $\delta_i$ are numbers of which the average is zero. The nearest neighbour coupling $J$ is
modulated by the $\delta_i$. Frustrating next-nearest neighbour coupling $\alpha J$ is also considered. The spring constant $K$ measures the elastic energy of a given distortion. Without magnetic field the spin chains are very susceptible towards dimerization $\delta_i = (-1)^i \delta$. The energy lowering due to dimerization is anomalously large $\Delta E \propto -\delta^{4/3}$ overcompensating the energy loss in elastic energy $\propto \delta^2$ [16].

Applying a magnetic field to the dimerized (D) phase of a spin-Peierls system ($T$ small) leaves the D phase unchanged until the critical field $H_c$ is reached. The stability stems from the singlet-triplet gap $\Delta_{\text{trip}}$. Hence an upper bound for $H_c$ is $g\mu_B H_c = \Delta_{\text{trip}}$. In fact, the critical field $H_c$ is smaller. Its Zeeman energy represents only 80% of the gap $\Delta_{\text{trip}}$ because the modulation also changes above the critical field. The system enters the incommensurably modulated phase.

1 Sinusoidal Modulation

Elastic X-ray scattering confirmed [14] that the distortion in the I phase is incommensurate. The deviation from dimerization $|q - \pi|$ increases with increasing magnetic field. This can be illustrated in the unfrustrated XY model which corresponds via the Jordan-Wigner transformation to free fermions. The susceptibility towards distortion becomes maximum at $q = 2k_F$ since $q = 2k_F$ allows to create particle-hole pairs of vanishing energy. A distortion with $q = 2k_F = 2\pi m + \pi$ is formed where $m$ is the magnetization. Since this distortion couples the degenerate states at $-k_F$ and at $k_F$ a gap appears there. Let us now gradually increase the interaction corresponding to the $S_i^z S_{i+1}^z$ terms at fixed particle number. For continuity no state can cross the gap such that the picture of a distortion at $2k_F$ remains valid [13, 18]. So we have

$$|q - \pi| = 2\pi m .$$  (1.2)
This relation is confirmed numerically [15].

Since experimentally it turned out that higher harmonics of the distortion are considerably suppressed it is plausible to start with \( q \) given by (1.2) [18]

\[
H = J \sum_i \left[ 1 - \delta \cos(qr_i) \right] S_i S_{i+1} .
\]  

(1.3)

The distribution of the local magnetizations \( m_i = \langle S_i^z \rangle \) is found from NMR experiments [11, 12]. With some success, the experimental data were compared to a continuum theory [8]. This theory, however, is based on a Hartree-Fock treatment where all Hartree and Fock terms are spatially constant. In Ref. [18] it is shown that this is a too crude approximation reducing the physics to the one of a XY chain. The antiferromagnetic correlations found in this way are much smaller than those of an isotropic XYZ chain. This conclusion is corroborated by several works [13, 20, 14]. But the spin isotropy of cuprates can hardly be questioned. To account for the smaller amplitudes it is proposed [18, 13] that experimentally only an effective magnetization \( m_i^{\text{eff}} \) is seen which is an average

\[
m_i^{\text{eff}} = (1 - 2\gamma)m_i + \gamma(m_{i-1} + m_{i+1}) .
\]  

(1.4)

The results for \( \gamma = 0.2 \) agree well with experiment [18]. The microscopic origin of the average is discussed in Sect. 4.

The reason for strong local magnetizations around the zeros of the modulation (cf. Fig. 2) is found in the localization of a spinon. Each zero binds exactly one spinon [14]. Summing the \( m_i \) around a magnetization maximum yields \( 1/2 \).

The order of the transition \( D \rightarrow I \) can be determined by investigating the ground state energy \( E(m) \) as function of the average magnetization \( m \) [13]. By means of a Legendre transformation \( \tilde{E}(h) = E(m) - hm \), one obtains the dependence of ground state energy \( \tilde{E}(h) \) on the magnetic field \( h = g\mu_B H \). It is found that a discontinuous jump for \( m \rightarrow 0 \) occurs. This implies that the transition \( D \rightarrow I \) for fixed sinusoidal modulation is of first order. The mean square of \( \cos(qr_i) \) jumps discontinuously from 1 to \( 1/2 \) if \( q \) deviates infinitesimally from \( \pi \) [15] since the \( r_i \) are summed over integer values only.

Experimentally, however, the observed first order jumps are much lower than those found for fixed sinusoidal modulation [21, 10, 11, 22, 23].

### 2 Adaptive Modulation

Since it was stated above that sinusoidal modulation alone does not account for the weak first order \( D \rightarrow I \) transition we turn to the full minimization of the ground state energy of (0.1). Derivation with respect to \( \delta_i \) yields

\[
0 = \langle S_{i+1}S_i \rangle - \langle \langle S_{j+1}S_j \rangle \rangle + K\delta_i ,
\]  

(2.5)
where $\langle\langle\cdot\rangle\rangle$ stands for the expectation value and the average along the chain. The double-bracketed term accounts for the constraint of the vanishing average of the $\delta_i$. The minimization is done iteratively [19, 15, 13].

The generic result is depicted in Fig. 2. The local magnetizations do not display major differences to the results for sinusoidal modulation in [18] because the spinon localization is in essence determined only by the slope with which the modulation vanishes. Note that the envelope of $m_i$ is proportional to the probability of finding a spinon at that site [14]. Hence, the magnetic part of the soliton displays localization as for sinusoidal modulation. For the distortions the relation (2.5) implies that the deviations from constantly alternating dimerization are also localized.

The distortion belonging to an isolated soliton is a kink, i.e. the distortion between two solitons resembles the one in the D phase. This implies a crucial advantage over the sinusoidal modulation. For kink-like solitons the reduction of the mean square distortion is proportional to the soliton number. Hence, a low soliton concentration leads only to a small change of the energy such that $E(m)$ is continuous (in the sense of Lipschitz) on $m \to 0$ [15].

The investigations in Ref. [15] of the model (0.1) yielded a continuous phase transition even though the magnetization grows very quickly above the critical field $m \propto -1/\ln(H-H_c)$. Most of the results of the continuum theories comply also with a phase transition of second order [3, 4, 7, 8]. Solely Horovitz mentions the possibility of soliton attraction in an early work [8] implying a first order transition. Buzdin et al. expect a first order transition at $T > 0$ [7].

In fact, the details of the models matter. Cross [24] argued already that an
elast energy with dispersion $K(q)$ being minimum at $q = \pi$ leads to a first order transition. The positive curvature of $K(q)$ around $q = \pi$ suppresses higher harmonics in the distortion. Hence, sinusoidal modulation is favoured. The concomitant concavity in $E(m)$ at low magnetization $m$ implies phase separation via the Maxwell construction. So the phase transition is first order \cite{13}. This finding is in accordance with the conclusion from a phenomenological Ginzburg-Landau description \cite{25} that the D $\rightarrow$ I transition is generically of first order.

At the transition the distance between two solitons is rather large so that the difference between sinusoidal and adaptive modulation matters most. At higher soliton concentrations the adaptive modulation becomes more and more sinusoidal but with a concentration dependent amplitude. The mean square distortion could be determined from the elastic lattice constants. These experimental results agree well with the predictions based on the model \cite{01}, see \cite{26}.

The continuum theories applying to the isotropic Heisenberg chain \cite{4,27} provide the following results (details in Ref. \cite{13}; $sn, cn, dn$: elliptic Jacobi functions)

$$m_i = \frac{W}{2}\left\{ \frac{1}{R} \ln \left( \frac{r_i}{k_m \xi_m} \right) + (-1)^i \cn \left( \frac{r_i}{k_m \xi_m}, k_m \right) \right\} \quad (2.6)$$

$$\delta_i = (-1)^i \delta \sn \left( \frac{r_i}{k_d \xi_d}, k_d \right) \quad (2.7)$$

with $\xi := \xi_m = \xi_d \Leftrightarrow k := k_m = k_d \quad (2.8)$

$$1 = 4mk_m/k_d K(k_m/d)\xi_m/d \quad (2.9)$$

$$1 = \pi k_m \xi_m \frac{W}{R} \quad (2.10)$$

The fits in Fig. 2 are based on Eqs. (2.6,2.7). Identity (2.8) is \textit{not} complied with, see Sect. 3. Otherwise no agreement would be obtained. Relation (2.9) is imposed on the fits whereas Eq. (2.10) serves as check. It is fulfilled within 4%.

The fact that $\xi_d/\xi_m \approx 1.33$ is considerably above unity complies nicely with the experimental findings. Elastic X-ray scattering \cite{10} found $\xi_d = 13.6 \pm 0.3$ while the NMR investigations provide $\xi_m \approx 10$ \cite{12} close to the transition.

There is also another way to introduce solitons in a spin-Peierls system than the application of magnetic field. Doping non-magnetic impurities in a spin-Peierls systems cuts the infinite chains into finite chain segments \cite{28}. In a number of works \cite{29} it has been shown that each impurity frees one spinon which is situated either before or after the impurity on the chain. Assuming a fixed dimerization it is easy to see that the spinon is bound to its generating impurity \cite{14} in accordance with experimental results \cite{30,31}.

But in a spin-Peierls system the change of the modulation has to be taken into account, too. This is done by introducing

$$H = J \sum_{i \geq 0} \left[ (1 + \delta_i)S_iS_{i+1} + \alpha S_iS_{i+2} + \frac{K}{2} \delta_i^2 + f \delta_i(-1)^i \delta_{\text{bulk}} \right] , \quad (2.11)$$
such that the impurity is at site -1. The important amendment compared to \( H \) in Eq. (1.1) is the last term. If the spinon moves away from the impurity the distortion pattern is changed between impurity and spinon. Due to an elastic interchain interaction (parametrized by \( f \)) a coherent distortion pattern throughout the whole three-dimensional system is preferred. A deviation from this pattern is energetically unfavourable. So one is led to include the last term in Eq. (2.11) assuming that the adjacent chains are dimerized as in the unperturbed D phase. The relation \( K = K_0 + f \) ensures the consistency of the distortion amplitude with its bulk value.

Fig. 3 displays the results for various elastic interchain interactions. The soliton is not localized at the impurity but at a certain distance. For lower \( f \) values the soliton resembles very much the ones in the I phase (cf. Fig. 2). On increasing \( f \) the soliton is squeezed more and more towards the impurity. Analogous results can be found by QMC [32], too.

Sure enough, the soliton is bound to the impurity confirming previous ideas [28, 31]. Moreover, the first excitations for the same distortions and in the same spin sector are found below the singlet-triplet gap at 52% of \( \Delta_{\text{trip}} \) for \( f = 0.01 \) and at 64% for \( f = 1.00 \). This matters for the spectroscopic analysis.

3 Local Renormalization

Most remarkable is the difference between the distortive soliton width \( \xi_d \) and the magnetic soliton width \( \xi_m \) in the numerical results (cf. Fig. 3). It amounts to 30% at \( \alpha = 0.35 \) depending mainly on the frustration for low soliton concentrations [33]. The challenge is to extend the existing continuum description to account for
this fact. Let us revisit the semiclassical treatment of the bosonized description of the spin-Peierls problem \[4\]. Minimizing the total energy the variation of the distortion \(\delta(x)\) leads to

\[
\delta(x) \propto e^{-2\sigma} \cos(2\phi_{\text{class}}) \tag{3.12}
\]

where \(\sigma := \langle \hat{\phi}^2 \rangle\) denotes the renormalizing fluctuations of the local bosonic field \(\hat{\phi}\) about the classical field \(\phi_{\text{class}}\). A soliton corresponds to a solution where \(\phi_{\text{class}}\) increases by \(\pi\) in a kink-like fashion. If \(\sigma\) is assumed to take the spatially constant value that it has in the ground state \[4\] one obtains

\[
\delta(x)/\delta = \cos(2\phi_{\text{class}}) = \tanh(x/\xi), \tag{3.13}
\]

wherein \(\xi\) is given by the ratio \(v_S/\Delta_{\text{trip}}\) of the spin wave velocity and the gap. The alternating component of the magnetization \(a(x)\) is proportional to \(\sin(2\phi_{\text{class}})\).

Hence, one has

\[
a(x) \propto \sqrt{1 - \tanh^2(x/\xi)} = 1/\cosh(x/\xi).
\]

But the presence of the soliton induces a deviation \(\Delta\sigma\) from its ground state value. Fig. 4 displays a generic result for this deviation. It is calculated on top of the solution of Nakano and Fukuyama \[4\]. The alternating component

\[
a(x) \propto \sqrt{1 - \exp(4\Delta\sigma) \tanh^2(x/\xi)} \tag{3.14}
\]

is thus indeed narrower than before due to the spatial dependence of the renormalization factor. The result in Fig. 4 is only a first step since the influence of the altered magnetic behaviour is not included. Yet it is clear that the renormalization is a local quantity and that this is the origin of the difference between \(\xi_d\) and \(\xi_m\).
4 Phasons

In Sect. 1 the discrepancy between theoretical and experimental amplitudes of the alternating local magnetizations was solved by an averaging procedure (1.4). Passing to adaptive modulations does not change the amplitudes much [13]. Hence, one still has to find the microscopic origin for the averaging.

Non-adiabatic effects are in fact responsible. The soliton lattice oscillates about its equilibrium positions. These oscillations are best understood in a continuum description which is well justified if the typical length $\xi$ is noticeably larger than the lattice constant. In such a continuum description the modulation $\delta(x)$ can be shifted along the chains without energy cost. This continuous translational invariance is spontaneously broken by the soliton lattice. Hence, there are massless Goldstone modes, the so-called phasons. They are analogous to the phonons of a crystal lattice except that they do not have three branches but only with one. While the atoms of a crystal lattice can be shifted in all three spatial directions the solitons can be shifted only along the chains.

Albeit the ideal spin-Peierls system is magnetically one-dimensional the distortions on different chains are elastically coupled. Thus, the phasons are governed by a 3D, though anisotropic, dispersion. The dispersion parameters are determined from the anisotropy of the correlation lengths assuming a Ginzburg-Landau description [25]. The corresponding $T^3$ term in the specific heat has been measured [33] and theory and experiment agree astonishingly well [25].

The zero point motion and the excited motion of phasons lead to the averaging (1.4). Let us denote the adiabatic result for the local magnetizations by $m_i = a(r_i) \cos(\pi r_i) + u(r_i)$ where $r_i$ is the component along the chains, $a(r_i)$ the alternating component and $u(r_i)$ the uniform component of the magnetizations. A local shift can be implemented by replacing $\pi r_i \to \pi r_i + \hat{\Theta}(r_i)$ where $\hat{\Theta}(r_i)$ denotes a phase shift operator. On the long time scales of a NMR measurement one measures

$$m_i^{\exp} = \langle m_i \rangle = a(r_i)\gamma' \cos(\pi r_i) + u(r_i)$$

(4.15)

with $\gamma' := \exp\left(-\frac{1}{2N} \sum_i \langle \hat{\Theta}^2(r_i) \rangle \right) < 1$. So there is an amplitude reduction engendered by the local fluctuations. The factor $\gamma'$ is comparable to a Debye-Waller factor.

Using the values fixed previously [22] yields $\gamma' = 0.16 \exp(-T/T^*)^2/2$ with $T^* \approx 16.9$K [3]. Eq. (1.4) is retrieved by estimating $a(r)$ and $u(r)$ from the discrete values $m_i$ by $a(r_i) = m_i/2 - (m_{i-1} + m_{i+1})/4$ and by $u(r_i) = m_i/2 + (m_{i-1} + m_{i+1})/4$. Inserting these formulae into Eq. (1.11) yields Eq. (1.4) with $\gamma = (1 - \gamma')/4$. At $T = 0$, $\gamma$ takes the value 0.21 in accordance with experiment [18] [13].
5 Conclusions

In this report the modulated phases of spin-Peierls systems were discussed. Such modulations are induced either by magnetic field or by impurities. In both ways the singlet pairing in the D phase is broken and spinons are freed. The lattice distortion adapts to the spinon by forming a zero to which the spinon is bound. This new entity constitutes the spin-Peierls soliton.

The order of the transition D → I phase on increasing field depends on model details. Imposed sinusoidal modulation leads to a pronounced first order transition. Allowing the system to choose an optimum modulation makes the transition continuous if the elastic energy is wave vector independent. If the elastic energy itself pins the modulation to $\pi$ a weak first order transition is found.

Doping induced solitons are bound to their generating impurity. The distortion pattern between impurity and soliton is not coherent with the bulk pattern. This costs energy which acts as a confining potential. Binding occurs for which experimental evidence exists [30, 31].

The difference between magnetic and distortive soliton width could be traced back to the so far neglected spatial dependence of the renormalizing local fluctuations. A fully self consistent analysis is in progress.

The reduction of the alternating magnetic amplitude due to phasons provides striking evidence for the importance of the lattice dynamics. The inclusion of non-adiabatic effects on top of an otherwise adiabatic calculation might still be unsatisfactory. So other approaches to non-adiabatic behaviour should be extended to the I phase [34].

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