

**Diploma** Thesis

# Non-conventional spin-Peierls phase in titanium oxyhalogenides

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# 1 Abstract

Low-dimensional S = 1/2 quantum spin systems are a fascinating playground for theoretical and experimental solid state research. These systems are strongly correlated and exhibit magnetic order in a variety of ground states. A multitude of degrees of freedom such as charge, spin, orbital and lattice degrees of freedom may be involved. The reduction of the spatial degrees of freedom to one or two space direction leads to interesting phenomena at low temperatures and their coupling to the crystal lattice may imply a breaking of certain symmetries. Furthermore, quantum fluctuations play a more important role than in higher-dimensional systems.

Especially frustrated systems are interesting, where competing interactions favor different magnetic ground states and where exotic phase transitions can be observed.

A very fascinating phenomenon is the Peierls instability of quasi one-dimensional metals against a lattice modulation with a modulation wave vector  $2k_F$ , the doubled Fermi wave vector [1, 2]. For an electronic system with partly filled conduction band it is energetically favorable to reduce the crystal symmetry and to open an energy gap at the Fermi edge. The energy cost due to the lattice deformation is overcome by the gain of electronic energy due to the reduction of the Brillouin zone and the corresponding energetic lowering of the occupied states nearby the Fermi edge. In case of half band filling, the Peierls-instability leads to a dimerization of the system, i.e., to a doubling of the unit cell and, therewith, a breaking of the translation symmetry.

Since one-dimensional Fermi operators can be mapped on spin operators via Jordan-Wigner transformation [3], an analogous phenomenon is expected to appear in one- dimensional spin systems. The possibility of the existence of such a spin-Peierls instability has been discussed already in the sixties. Indeed, in 1975, Bray *et al.* [4, 5] observed a spin-Peierls transition from a quasi one-dimensional spin S = 1/2 chain coupled to the lattice to a dimerized non-magnetic ground state in the organic compounds TTFCuS<sub>4</sub>C<sub>4</sub>(CF<sub>3</sub>)<sub>4</sub> and TTFCuBDT. With CuGeO<sub>3</sub> the first inorganic spin-Peierls compound was found in 1993 [6]. Since then the understanding of spin-Peierls systems has substantially deepened.

In recent years the titanium oxyhalogenides became subject to research as they are believed to be another inorganic spin-Peierls compound. However, there are some experimental facts, which go clearly beyond a canonical spin-Peierls scenario, suggesting even richer physics in these compounds.

In canonical spin-Peierls systems, there is a single second order phase transition to a dimerized ground state. Applying sufficiently high magnetic fields leads to a phase transition to an incommensurably modulated phase [7].

#### 1 Abstract

In the titanium oxyhalogenides there are two successive phase transitions with incommensurate superstructure satellites appearing inbetween in absence of a magnetic field. Unlike in the canonical scenario, the low temperature phase transition is found to be of first order [8].

Rückamp *et al* [9] ruled out that strong orbital fluctuations are responsible for the observed deviations from canonical spin-Peierls behavior. Instead, they proposed the frustration of interchain interactions, inherent to the bilayer structure of titanium oxyhalogenides, to be responsible for the observed incommensurability.

In the Ginzburg-Landau expansion for the free energy up to second order in the order parameter, i.e., the displacement of the Ti ions along the spin chains, the interchain frustration gives rise to terms which favor a minimum with an incommensurate modulation. With decreasing temperature the amplitudes of the displacements grow and a commensurate order is favored. However, this is not described in the second order expansion.

The aim of the present thesis is to extend the Landau expansion up to fourth order, which allows us to capture the lock-in transition to the commensurate phase in quantitative terms. The minimization of the Landau functional is realized numerically.

In order to deepen the understanding of the driving forces for the phase transitions, a one-dimensional model of two frustrated spin chains is discussed though the real system is two-dimensional and a large number of chains has to be investigated.

Chapter 2 gives a brief introduction in crystalline solid state physics with a focus on lowdimensional quantum spin systems and the one-dimensional spin S = 1/2 Heisenberg chain in particular. Furthermore, the canonical spin-Peierls scenario will be discussed. Particular attention will be directed to the existence of incommensurably modulated phases, which can be discussed as soliton lattices.

Chapter 3 overviews the physics of the titanium oxyhalogenides and reports on experimental data concerning the commensurate and incommensurate phases at low temperatures and the phase transition inbetween, as well as theoretical approaches to explain the nature of the incommensurate phase and to study the driving forces for the phase transitions.

The main part of the thesis, Chapter 4, deals with the extension of the above mentioned phenomenological model by Rückamp *et al* [9] by including the fourth order terms in the Ginzburg-Landau expansion for the free energy. In the first part of Chapter 4, the simplified one-dimensional model of two frustrated spin chains is discussed in detail with regard to the modulation of the displacements in the commensurate and incommensurate phase and to the incommensurability along the chains in particular.

Furthermore, it is described how the free parameter in the model can be adapted in order to reproduce experimental data. A detailed discussion of the obtained results follows in the second part of Chapter 4. In particular, the modulation of the displacements close to the incommensurate-commensurate phase transition and the corresponding energies are discussed within a soliton lattice scenario.

Finally, a summary of the results is presented in Chapter 5, as well as an outlook on possible extensions of this work.

# 2 Introduction

# 2.1 From crystalline solids to antiferromagnetic quantum spin systems

Crystalline solids consist of a periodic structure of atoms whose atomic orbitals form energy bands due to the overlap of the atomic wave functions. The physical properties of crystalline materials are determined by the filling of these energy bands with valence electrons [10, 11, 12, 13].

In band insulators there is a gap between the fully filled valence band and the unoccupied conduction band. In semiconductors this gap can be overcome by thermal excitation. In metals there is no gap and an odd number of electrons per unit cell implies a half filled top band. Therefore, metals are good conductors. However, in some materials the interaction between the electrons leads to an insulating behavior.

So called *Mott-Hubbard* insulators [14, 15, 16, 17] can be described by the Hubbard model with half filling

$$H = -t \sum_{\langle i,j \rangle,\sigma} c^{\dagger}_{i,\sigma} c_{j,\sigma} + U \sum_{i} \left( n_{i,\uparrow} - \frac{1}{2} \right) \left( n_{i,\downarrow} - \frac{1}{2} \right) , \qquad (2.1)$$

where *i* and *j* are the lattice indices of nearest neighbor atoms. The operators  $c_{i,\sigma}^{\dagger}(c_{j,\sigma})$  create (annihilate) an electron with spin  $\sigma$  at site *i*. The operator  $n_{i,\sigma} = c_{i,\sigma}^{\dagger}c_{j,\sigma}$  is the occupation number operator [18, 19, 20, 21].

The *t*-term in (2.1) describes the energy gained from next neighbor hopping with the hopping amplitude *t*, while the *U*-term disfavors hopping due to the Coulomb repulsion *U* between two electrons sitting on the same site. If the system becomes insulating, depends on the ratio U/t. Due to the interaction between the electrons, the half filled band splits up in a lower ( $\epsilon$ ) and an upper ( $\epsilon + U$ ) Hubbard band, where  $\epsilon$  is the atomic energy. For sufficiently high Coulomb repulsion *U* there is only one electron on each site and the system becomes a *Mott-Hubbard* insulator [22].

In the low energy sector the remaining degrees of freedom are the magnetic degrees of freedom of the electronic subsystem, i.e., the spin of the electrons.

In second order perturbation theory in the limit of vanishing hopping, the effective model is the spin isotropic antiferromagnetic Heisenberg model with an exchange constant

 $J = 4t^2/U > 0$  and spin S = 1/2 vector operators  $\mathbf{S}_i$  on site *i* [21, 23]:

$$H = J \sum_{\langle i,j \rangle} \mathbf{S}_i \mathbf{S}_j \tag{2.2}$$

Since we are mainly interested in the discussion of low-dimensional quantum spin systems, we will discuss the anisotropic Heisenberg model in the following.

### 2.2 Low-dimensional quantum spin systems

In anisotropic systems with arbitrary spin size, the Hamiltonian 2.2 generalizes to:

$$H = \sum_{\langle i,j \rangle} J_{i,j} \mathbf{S}_i \mathbf{S}_j \tag{2.3}$$

This Heisenberg Hamiltonian describes a quantum antiferromagnet, whose properties depend on the dimension of the underlying lattice or rather on the coordination number  $Z^{1}$ , on the spin size *S* and on the frustration of the exchange interaction.



Fig. 2.1: (a) In the square lattice the interaction between the sublattices is pure antiferromagnetic, while possible interaction on the gray (black) sublattice would be pure ferromagnetic. (b) The unfrustrated triangle lattice without antiferromagnetic interactions on the gray (black) sublattice. (c) The frustrated triangle lattice with an antiferromagnetic coupling on the black sublattice. (Antiferromagnetic interactions are displayed as solid lines and ferromagnetic interactions as dashed lines.)

Frustration is an effect which occurs whenever competing interactions favor different magnetic ground states. In frustrated antiferromagnetic systems, it is not possible to separate the spins in *A*-spins and *B*-spins so that possible interactions on the *A*- or *B*-sublattice are pure ferromagnetic, while interactions between *A*- and *B*-spins are pure antiferromagnetic. If there are any antiferromagnetic interactions on the *A*- or *B*-sublattice, there is no classical spin orientation which can fully satisfy both interactions and the system becomes frustrated.

<sup>&</sup>lt;sup>1</sup>In d-dimensional hypercubic lattices the coordination number is Z = 2d.

In some materials, the exchange  $J_{i,j}$  is strongly anisotropic and can be neglected in one or even two space directions. The one-dimensional Heisenberg model

$$H = J \sum_{i} \mathbf{S}_{i} \mathbf{S}_{i+1} \,. \tag{2.4}$$

gives an appropriate description of low-dimensional spin systems such as spin-Peierls matters CuGeO<sub>3</sub> [6],  $\alpha'$ -NaV<sub>2</sub>O<sub>5</sub> [24] and the titanium oxyhalogenides [25, 26].

# 2.3 Néel and RVB states



Fig. 2.2: (a) *Néel* state for the square lattice. (b) Possible singlet product state as a component of the *RVB* state for the square lattice.

In mean field theory, quantum fluctuations are neglected, i.e., the vector operators  $S_i$  are treated as classical vectors. In this approximation, the ground state for unfrustrated systems is the so called *Néel* order, where neighboring spins on sublattices *A* and *B* are antiparallel to each other (see Fig. 2.2a). In general, all states with finite sublattice magnetization  $\langle S_A \rangle - \langle S_B \rangle \neq 0$  are called *Néel* states.



Fig. 2.3: The so called *Goldstone bosons* are the gapless low energy excitations of the spin rotation symmetry breaking *Néel* state

*Néel* states have a long-range order, which spontaneously breaks the spin rotation symmetry. Excitations of the ground state are realized by rotations of the spins, corresponding to a change of the *z*-component of the total spin ( $\Delta S_z = \pm 1$ ). The energy loss due to such

#### 2 Introduction

long-wave distortions, the so called *massless Goldstone bosons*, is very small since locally the order of the spins is still antiferromagnetic (see Fig. 2.3).

Another possible ground state is the *Resonating Valence Bond* (*RVB*) state proposed by Anderson [27], where all spins combine pairwise to singlets. The corresponding wave function is a weighted linear superposition of all possible singlet product states.

*RVB* states have no long-range order or sublattice magnetization. In contrast to *Néel* states, the excitations of *RVB* states are not gapless due to the energy needed for breaking the singlets. However, if the range of the singlets is not finite, the energy gap disappears and a distinction between *Néel* and *RVB* states becomes ambiguous [28].

The energy of the pure classical *Néel* state and the energy of a component of the *RVB* state, i.e., the energy of a singlet product state as shown in Figure 2.2b, are variational estimates for the corresponding ground state energies. A comparison of the energy per spin in the classical *Néel* state ( $E_{N\acute{e}el} = -S^2ZJ/2$ ), and the *RVB* state on the other hand ( $E_{RVB} = -S(S+1)J/2$ )<sup>2</sup>, shows that systems with large coordination number *Z*, and large spin size *S* favor *Néel* order, while frustration operates weakening on that order as antiparallel spin orientation cannot be fully satisfied in frustrated systems (see Fig. 2.4).



Fig. 2.4: Frustration disfavors *Néel* order since an antiparallel spin orientation is suboptimal.

# 2.4 Unfrustrated antiferromagnetic spin S=1/2 Heisenberg chain

The one-dimensional unfrustrated spin S = 1/2 Heisenberg chain is an exactly solvable gapless system with quasi long-range correlations [29, 30, 31, 32]. Therefore, it is often illustrated in *Néel* order, although that is not the exact ground state [33].

The spin chain does not allow a finite sublattice magnetization at T = 0 [34]. At finite temperatures, a long-range magnetic order is not established in one-dimensional quantum spin systems due to the theorem of Mermin and Wagner [35, 36], which says that in one- and two-dimensional systems the classical ground state is destroyed by bosonic fluctuations.

<sup>&</sup>lt;sup>2</sup>The energy per spin in a singlet product state is independent of the coordination number. In a ddimensional hypercubic lattice with N sites, the singlet state profits independently of the dimensionality from N/2 spin pairs.

In the lack of sublattice magnetization and the strong local singlet character of the wave function, the ground state of the one-dimensional spin S = 1/2 Heisenberg chain even resembles *RVB* states. The real ground state is a complicated superposition of *Néel*like and *RVB*like states. However, for a phenomenological description both pictures are suitable.



Fig. 2.5: Illustration of a S = 1/2 spinon as a domain wall in a) *Néel* or b) *RVB* states.

Excitations from the ground state are the so called spinons. A spinon can be illustrated as a domain wall between two ground state pattern (see Fig. 2.5). It is easy to see that spinons are spin S = 1/2 objects. They are asymptotically free, i.e., for large distances they can roam freely on the Heisenberg chain [33]. On chains with an even number of spins and with periodic boundary conditions, spinons have to be created in pairs (see Fig. 2.6) [37].



Fig. 2.6: For an even number of spins and for periodic boundary conditions, the creation of a single spinon automatically leads to the creation of a second spinon.

Note that the spinon picture is only suitable for one-dimensional systems. In higher dimensions, domain walls are (d - 1)-dimensional objects with an energy proportional to  $L^{d-1}$ . <sup>3</sup> Therefore, spinons are no longer elementary excitations.

 $<sup>^{3}</sup>$  *L* is the linear expansion of the system.

#### 2.4.1 Spin-Peierls transition

In case of half band filling, the Peierls-instability of a quasi one-dimensional metal against a lattice modulation with a modulation wave vector  $2k_F$ , the doubled Fermi wave vector, leads to a dimerization of the system, i.e. to a doubling of the unit cell and, therewith, to a breaking of the translation symmetry [1].

Since one-dimensional Fermi operators can be mapped on spin operators via Jordan-Wigner transformation [3], an analogous phenomenon appears in one-dimensional spin systems, the so called spin-Peierls systems.

Spin-Peierls systems are quasi one-dimensional antiferromagnetic spin systems coupled to the lattice or to the three-dimensional degrees of freedom of the phonon system, respectively. At low temperatures, these systems experience a spontaneous lattice distortion and undergo a second order phase transition to a dimerized non-magnetic ground state. In the dimerized phase, spins on neighboring sites form singlets, i.e., the distance between neighboring spins is alternately enlarged and reduced compared to the uniform phase, where all distances are equidistant [4, 2].

Since the magnetic exchange is strongly dependent from the spin-spin distance, the magnetic energy of the system is reduced compared to the non-dimerized phase, while the elastic energy certainly increases. The susceptibility of the magnetic system, which indicates to what extent the energy can be reduced, even diverges for a distortion with a modulation wave vector  $q = \pi$  [4].

If only small displacements, i.e., low phonon energies, are taken into account, we can describe the phonons in harmonic approximation as non-interacting bosons and we can consider a linear coupling between the phonons and the spin system. In mean field theory, i.e., if the dynamics of the phonons are neglected, the dimerization can be described by the dimensionless static distortion  $\Phi_0$ . The Hamiltonian in adiabatic approximation can be written as

$$H = J \sum_{i} \left[ (1 + (-1)^{i} \Phi_{0}) S_{i+1} S_{i} + \frac{K_{0}}{2} \Phi_{0}^{2} \right] , \qquad (2.5)$$

where  $K_0$  is the spring constant of the phonon system. As we can see nicely in (2.5), the magnetic exchange alternates between  $J(1 + \Phi_0)$  on the even bonds and  $J(1 - \Phi_0)$  on the odd bonds (see Fig. 2.7). If the dimers are on the short bonds or on the long bonds, depends on the specific properties of the system.

Cross and Fisher showed that the energy gain of the magnetic system is proportional to  $\Phi_0^{4/3}$ . For sufficiently small dimerizations  $\Phi_0$ , it overcompensates the energy loss due the elastic distortion, which increases only with  $\Phi_0^2$ , independently of prefactors [38].

While in one-dimensional systems the favor of the dimerized phase is quite obvious, the response of the ground state energy to dimerization in two-dimensional magnetic systems is much weaker ( $\propto -\Phi_0^2$ ) and it depends on prefactors if it still outweights the loss in elastic energy.



Fig. 2.7: Spin-Peierls distortion with dimers on the short bonds.

In two-dimensional systems, it is even possible to have a finite dimerization as well as a long-range magnetic order, which is reduced, but not destroyed as in one-dimensional systems [39].

#### 2.4.2 Incommensurably modulated phases

Because a certain energy is needed to break the singlets in the dimerized phase, the system is not gapless anymore. Therefore, it is stable against not too large magnetic fields. However, if the magnetic field exceeds a critical value  $H_c$ , the Zeeman energy is high enough to yield the excitation energy  $\Delta_{trip}$  for a spinon and an incommensurably modulated phase occurs. In this phase the spin-spin distance now varies from site to site. In fact, the system enters the incommensurably modulated phase already for a magnetic field with a Zeeman energy of  $g\mu_B H_c \geq 0.8\Delta_{trip}$  [40] because above the critical field the modulation changes as well.

The incommensurability  $\delta = |q - \pi|$ , i.e., the deviation of the modulation wave vector q in the incommensurably modulated phase from  $q = \pi$  in the commensurably modulated dimerized phase, increases with increasing magnetic field [41].

Since a spinon is always bounded to a zero of the modulation, which is indicated by strong local magnetizations at the zeros of the distortion (see Fig. 2.8), the number of spinons also increases with increasing magnetic fields. The combination of such a zero and a spinon is from here on called a soliton.

For high soliton concentrations, i.e., not too close to the commensurate-incommensurate phase transition, the modulation is sinusoidal [42] and can be described by the following Hamiltonian

$$H = J \sum_{i} (1 - \Phi_0 \cos\left(qr_i\right)) \mathbf{S}_{i+1} \mathbf{S}_i , \qquad (2.6)$$

where *q* is the wave vector of the magnetic modulation.

For vanishing magnetization  $m \to 0$  the ground state energy E(m) has a discontinuity for infinitesimal small deviations from  $q = \pi$ , which leads to a first order phase transition between the incommensurate phase and the dimerized phase, where the modulation

wave vector "locks-in" to the commensurate value of  $q = \pi$ . This discontinuity occurs since the average of the squared sinusoidal distortion  $cos((\pi + \delta)r_i)$  jumps discontinuously from 1 to 1/2 for any finite value of  $\delta$  because the  $r_i$  are discrete.

Even though experimental data for the spin-Peierls compound CuGeO<sub>3</sub> characterize the phase transition to be of first order [43, 44, 45], the discontinuity is much smaller than suggested by the sinusoidal modulation.



Fig. 2.8: Adaptive solution for the local displacements  $\Phi_i$  and the local magnetizations  $m_i$  at sites *i*. (Figure taken from Ref. [40])

While the description with a sinusoidal modulation is suitable for high soliton concentrations, a self-consistent calculation of the distortions shows that an isolated soliton has a kinklike distortion (see Fig. 2.8), which suggests that close to the lock-in transition to the dimerized phase the pure sinusoidal modulation is not an adequate description [40].

The decay of the average of the squared distortions in a periodic soliton lattice is proportional to the soliton number and soliton width  $\xi$ . In the incommensurate phase, the formation of a domain wall becomes energetically favorable, while the mutual repulsion of the solitons makes the increase of their number a continuous function of the driving field. The elastic energy is wave vector independent and small soliton concentrations produce only a small change of the ground state energy.

This scenario leads to a continuous phase transition although the magnetization increases

exponentially steep with  $m \propto -1/\ln (H - H_c)$  [46].<sup>4</sup>

Cross [49] argued qualitatively that, if the elastic energy has a dispersion K(q), which favors a modulation with  $q = \pi$  itself, again a first order phase transition can be observed. In this scenario, a local attraction between the solitons exists, which can taken to be large in comparison to the repulsive interaction for very large inter-soliton spacings. The discontinuous jump in the magnetization can be arbitrary weak in dependence of the exact dispersion K(q), which could explain the weak first order transition observed in experiments [43, 44, 45].

Also Horovitz [50] proposed that soliton attraction is responsible for the observed first order character of the phase transition to the commensurate phase.

Analyzing the free energy of a soliton lattice within a phenomenological Ginzburg-Landau theory, Bruce *et al.* [51] showed that within a "single-plane-wave" approximation, i.e., if the ground state in the incommensurate phase consists of a single Fourier-component at the modulation wave vector minimizing the distortion energy, the phase transition is of first order, while an admixture of the Fourier-components might lead to a continuous phase transition.

We see that it depends strongly on the details of the model used for the description, if the first order character of the lock-in transition can be captured or not.

#### 2.4.2.1 Spatial dependence of the soliton excitations

In the following, it is shown how Nakano and Fukuyama [52] determined the spatial dependence of the displacement  $\Phi(x)$  for soliton excitations.

Using the Jordan-Wigner transformation [3], the spin variables of the one-dimensional S = 1/2 Heisenberg chain can be represented by interacting spinless fermions.

Cross and Fisher [38] treated in turn the interaction between the fermions by use of the bosonic representations of fermion operators [53, 54], which allows a semi-classical treatment. The problem of interacting fermions is mapped on an exactly solvable system of free bosons.

Starting from the Heisenberg Hamiltonian (2.4) without bond alternation, the Jordan-Wigner transformation leads to the follwing fermion Hamiltonian

$$H_0 = \sum_{k} J(\cos(ka) - 1) a_k^{\dagger} a_k + \frac{1}{N} \sum_{k,k',q} J\cos(qa) a_{k+q}^{\dagger} a_{k'-q}^{\dagger} a_{k'} a_k , \qquad (2.7)$$

with the lattice spacing *a*. The fermion operators  $a_k$  ( $a_k^{\dagger}$ ) create (annihilate) a fermion with momentum *k*. This Hamiltonian can be diagonalized by rewriting it in terms of density operators, based on the linearization of the cosine energy band and the transformation

<sup>&</sup>lt;sup>4</sup>There are several experiments showing the existence of such magnetic soliton lattices [47, 48]

of Tomonaga [55] and Mattis and Lieb [56]. Therewith, (2.7) can be transformed to the following phase Hamiltonian

$$H_0 = \int dx [A(\nabla \theta)^2 + Cp^2] , \qquad (2.8)$$

wherein the phase variable  $\theta(x)$  is defined as a linear combination of the density operators and p(x) as a spatial derivative of such a linear combination. *A* and *C* are constants proportional to the spin wave velocity.  $\theta(x)$  and p(x) satisfy the commutator relation  $[p(x), \theta(x')] = -i\delta(x - x')$ .

In the presence of bond alternations, the exchange interaction *J* is no longer uniform in space and the elastic energy of the displacement has to be considered, which leads to the following quantum sine-Gordon Hamiltonian for the ground state ( $\Phi(x) = \Phi_0$ ) in the absence of a magnetic field

$$H = \int dx [A(\nabla \theta)^2 - B\cos(\theta) + Cp^2 + 2K\Phi_0^2]$$
(2.9)

with  $B = \lambda J \Phi_0$  and the proportionality constant  $\lambda$ .<sup>5</sup>

A possible lowest excitation above the ground state is the formation of a soliton, which requires a spatial variation of the displacement  $\Phi(x)$  and, corresponding to that, a spatial variation of the average of the phase variable  $\theta(x) = \theta_s(x) + \hat{\theta}(x)$ .

Within a self consistent harmonic approximation the phase variable is separated into  $\theta_s(x)$ , the classical treatable sum of such an average, and the quantum fluctuations  $\hat{\theta}(x)$  around [57], which are treated in harmonic approximation, and the total Hamiltonian can be written as

$$H = \int dx \left[ A(\nabla \theta_s)^2 + A(\nabla \hat{\theta})^2 - D(x) \cos\left(\theta_s\right) \left( 1 - \frac{\hat{\theta}^2 - \langle \hat{\theta}^2 \rangle}{2} \right) + Cp^2 + 2K\Phi(x)^2 \right] + \int dx [2A\nabla \theta_s \nabla \hat{\theta} + D(x)\hat{\theta}(x) \sin\left(\theta_s\right)]$$
(2.10)

with  $D(x) = \lambda J \Phi(x) e^{-\langle \theta^2 \rangle/2}$ . Assuming that  $\sigma = \langle \hat{\theta}^2 \rangle$  is equal to the average in the ground state, i.e., it is uniform in space, and requirering that  $\theta_s$  satisfies the differential equation

$$2A\nabla^2\theta_s - D(x)\sin\left(\theta_s\right) = 0, \qquad (2.11)$$

assures that the second term of the r.h.s. of (2.10) vanishes for any  $\hat{\theta}(x)$ . Differentiating (2.10) with respect to  $\Phi(x)$  and using (2.11), leads to the following equation

$$\nabla^2 \theta_s - \frac{1}{2\xi^2} \sin\left(2\theta_s\right) = 0 \tag{2.12}$$

<sup>&</sup>lt;sup>5</sup>Differing from Ref. [52] the lattice spacing is considered as a = 1

with  $\xi = 2\pi / \lambda^2 \cdot K / J$ . The soliton solution of (2.12) corresponds to the following spatial dependence of the displacement

$$\Phi(x) = \pm \Phi_0 \cos\left(\theta_s\right) = \pm \Phi_0 \tanh\left(\frac{x}{\xi_{\Phi}}\right).$$
(2.13)

 $\Phi_0$  is the displacement in the ground state, i.e., for infinite large soliton-soliton distances  $(x \to \pm \infty)$ , and  $\xi_{\Phi}$  is the width of a soliton.

These kinklike solutions show that close to the lock-in transition to the dimerized phase, almost all spins are dimerized in presence of a finite number of spinons, which disappear in the fully dimerized spin-Peierls state.

The alternating component of the magnetization is proportional to the following spatial dependence

$$m_{alt}(x) \propto \sin(\theta_s) = \sqrt{1 - \tanh^2\left(\frac{x}{\xi_m}\right)} = \frac{1}{\cos\left(\frac{x}{\xi_m}\right)}.$$
 (2.14)

In this scenario the magnetic soliton width  $\xi_m$  is identical to the elastic soliton width  $\xi_{\Phi}$ .

However, DMRG-results [58], as well as experiments [41, 48, 59, 60], show a ratio  $\xi_{\Phi}/\xi_m$  which is about 30% higher than unity. Considering fluctuations on top of the Nakano/ Fukuyama solution, i.e., taking into account the spatial dependence of the phase variable  $\sigma = \langle \hat{\theta}^2 \rangle$  which deviates by  $\Delta \sigma > 0$  from its ground state, leads to an additional exponential factor  $e^{-\Delta \sigma/2}$  in the spatial dependence of the displacement and, therewith, to the following proportionality for the alternating component of the magnetization

$$m_{alt}(x) \propto \sqrt{1 - e^{-\Delta\sigma} \tanh^2\left(\frac{x}{\xi}\right)}$$
 (2.15)

This dependence is narrower than before, leading to a smaller value for  $\xi_m$  [40].

A fully self consistent calculation, which accounts for the fluctuations, was performed by Uhrig [58], corroborating the conjecture that the numerical finding  $\xi_m \neq \xi_{\Phi}$  is related to the spatial dependence of the phase variable.

2 Introduction

# 3 Physics of the titanium oxyhalogenides

Since the physics in the first inorganic spin-Peierls compound  $CuGeO_3$  is well described by now, there is a great interest in understanding other inorganic systems dominated by spin-Peierls physics. Due to strong spatial anisotropy, which leads to quasi one- dimensional magnetic interactions necessary for a spin-Peierls scenario, the titanium oxyhalogenides TiOCl and TiOBr seem to be good candidates for such a system.

In canonical spin-Peierls systems, there is a single second order phase transition to a dimerized ground state. Applying sufficiently high magnetic fields leads to a phase transition to an incommensurably modulated phase [7].

In the titanium oxyhalogenides, however, there are some experimental facts, which are not expected in a conventional spin-Peierls scenario: Already in zero magnetic fields, two phase transitions can be observed. The ground state at high temperatures is Mottinsulating and paramagnetic. With decreasing temperature, a phase transition to an incommensurably modulated phase occurs without applying a magnetic field. This second order phase transition is succeeded by a lock-in transition to a non-magnetic dimerized spin-Peierls state. The lock-in transition is of first order, in contrast to the second order spin-Peierls transition observed in conventional spin-Peierls compounds.

Although the titanium oxyhalogenides have an odd number of valence electrons, they do not show metallic behavior. Due to strong short range Coulomb interactions, they are *Mott-Hubbard* insulators with a charge gap of approximately 2 eV [9].

Taking into account the lowered dimension due to strong spatial anisotropy, they can be described by the one-dimensional antiferromagnetic Heisenberg model. While this description is valid at least at low temperatures, the temperature dependencies of optical reflectivity and angle-resolved photoelectron spectroscopy (ARPES) suggest that a crossover from two-dimensional towards a one-dimensional character of the magnetic interactions occurs on cooling from room temperature down to zero temperature [61].

# 3.1 Structure of the titanium oxyhalogenides

At room temperature, TiOCl and TiOBr crystallize in an orthorhombic structure of FeOCl type with Z = 2 atoms of each sort per unit cell [63], consisting of two-dimensional (2D) Ti-O bilayers within the ab-plane well separated by Cl/Br ions (see Fig. 3.1a). The Cl/Br ions mediate a weak van der Waals interactions between successive bilayers.

Within these bilayers titanium and oxygen ions form buckled chains in a-direction while



Fig. 3.1: (a) View along the b-direction on the structure of TiOCl. (b) Triangle structure of the Ti sublattice with next neighbor hopping integrals in a- and b-direction and geometric frustration of the coupling. (Figures taken from [62])

Compound	Ti-Ti <sub>b</sub>	Ti-Ti <sub>bc</sub>	t	ť
TiOCl	3.38	3.2	-0.21	0.04
TiOBr	2.49	3.19	-0.17	0.06

Tab. 3.1: Intra- and interchain Ti-Ti distances (in Å) and intra- and interchain hopping integrals t and t' (in eV) [62].

atoms of similar type form chains along the b-direction. The distance between Ti ions in different layers (Ti-Ti<sub>*bc*</sub>) turns out to be slightly shorter than the Ti-Ti distance within a layer (Ti-Ti<sub>*b*</sub>) (see Tab. 3.1) [62].

Furthermore, the layers are shifted against each other by half a lattice constant [64] so that the Ti S = 1/2 sublattice has the structure of almost equal-sided triangles, which leads to a geometric frustration of the antiferromagnetic coupling of the spins (see Fig. 3.1b).

Each Ti ion is surrounded by a distorted octahedron of O and Cl/Br ions. As the oxygen and chlorine bands lie well below the transition-metal *d* level, only the Ti 3*d* electrons are responsible for the electronic and thermodynamic properties of the titanium oxyhalogenides [65]. For perfect octahedral coordination, the crystal field already splits the fivefold degenerated 3*d* orbital into the lower-lying  $t_{2g}$  triplet ( $d_{xy}$ ,  $d_{xz}$ ,  $d_{yz}$ ) and the higher-lying  $e_g$  doublet ( $d_{x^2-y^2}$ ,  $d_{z^2}$ ) [26] (see Fig. 3.3).<sup>1</sup>

<sup>&</sup>lt;sup>1</sup>Set of axes has been chosen as: z = a and x and y axes are rotated by 45° relative to the b and c axes



Fig. 3.2: (a) Splitting of the fivefold degenerated 3*d* orbital due to the octahedral crystal field. (b)  $e_g$  doublet with  $d_{z^2}$  and  $d_{x^2-y^2}$  orbital. (c)  $t_{2g}$  triplet with  $d_{xy}$ ,  $d_{xz}$  and  $d_{yz}$  orbital. The octahedrons are formed by two Cl/Br (green, slightly bigger) and four O (blue) ions. (Figure taken from Ref. [66])

The distortion of the octahedron and the symmetry breaking due to different atom types lift the degeneracy of the triplet and doublet states. While the  $d_{xy}$  orbitals form linear chains in b-direction, mediated by direct exchange between Ti ions within a layer, the  $d_{xz}$  and  $d_{yz}$  orbitals form zigzag chains between Ti ions on different layers along the a-direction, mediated by superexchange via oxygens (see Fig. 3.3) [26].

LDA+U calculations identify the  $d_{xy}$  band as lower lying and slightly split off from the degenerated  $d_{xz}$  and  $d_{yz}$  bands [67]. In the ground state the 3*d* electrons occupy the  $d_{xy}$  orbital [25, 68]. Therefore, quasi-one-dimensional S = 1/2 chains are formed in b-direction, giving rise to strong direct exchange between Ti ions on different layers and negligible coupling in the other directions.

Indeed Zhang *et al.* [69] calculated within *ab initio* density-functional theory (DFT) by the Car-Parrinello projector-augmented-wave (CP-PAW) method a dominance of the coupling in b-direction  $J_b = 660.1$  K, compared to the coupling  $J_c = -16.7$  K and  $J_a = -10.5$  K in the other directions.



Fig. 3.3: (a) Ti sublattice with  $d_{xy}$  orbitals forming linear chains along b-direction. (b) Top view on the Ti sublattice with  $d_{xy}$  orbital chain. (c)  $d_{xz}$  orbitals forming zigzag chains along a-direction (The plane of the orbitals is tilted by 45° out of the paper so that two of the lobes point towards Ti atoms of the neighboring layer). (Figure taken from Ref. [66])

Because displacements of Ti ions due to phonon modulations are expected to influence the electronic structure and therefore the occupation of the *d* orbitals, it was proposed that orbital fluctuations may play a role. They could be responsible for the unconventional behavior of the titanium oxyhalogenides around  $T_{c2}$  [26, 25, 68, 70, 67, 61, 71, 72]. However, it was shown that there is no significant phonon-induced admixture of  $d_{xz}$  and  $d_{yz}$  orbitals to the ground state [8]. Furthermore, Rükamp *et al.* [9] showed that the orbital degree of freedom is actually quenched as the orbital excitation gap is of the order of 0.25 eV ( $\approx$  2900 K). As mentioned before, the charge gap is  $\approx$  2 eV.

For the explanation of the low energy physics in the titanium oxyhalogenides it is therefore sufficient to consider spin and lattice degrees of freedom.

## 3.2 Spin-Peierls like behavior

In a canonical spin-Peierls scenario a single second order phase transition is expected to appear at low temperatures related to a doubling of the unit cell and an opening of a spin gap. Applying sufficiently high magnetic fields yields the excitation energy for the solitonlike S = 1/2 states and therefore leads to an incommensurably modulated phase in conventional spin-Peierls compounds.

Several experimental facts imply the existence of a spin-Peierls phase transition in the titanium oxyhalogenides:

- a simultaneous lattice dimerization of the Ti ions below  $T_{c1} = 67$  K in TiOCl and  $T_{c1} = 27$  K in TiOBr accompanied by a steep decrease of the magnetic susceptibility
- the opening of a spin excitation gap of  $\Delta = 430$  K [70, 73] in TiOCl and  $\Delta = 149$  K in TiOBr [74] at  $T_{c1}$

However, the following experimental facts cannot be explained in a conventional spin-Peierls scenario:

- the existence of two successive phase transition at  $T_{c1} = 67$  K and  $T_{c2} = 91$  K in TiOCl and  $T_{c1} = 27$  K and  $T_{c2} = 48$  K in TiOBr
- the first order character of the low temperature phase transition
- the appearance of incommensurate super structure satellites between *T*<sub>c1</sub> and *T*<sub>c2</sub> in zero magnetic fields
- the observation of two inequivalent Ti sites in the low temperature regime
- the extraordinarily large ratio of the spin excitation gap  $\Delta$  to the dimerization temperature,  $2\Delta/T_{c1} \approx 12.83$  (TiOCl) [4] and  $2\Delta/T_{c1} \approx 11.03$  (TiOBr) [74], compared to  $2\Delta/T_{c1} \approx 3.53$  [7] in conventional spin-Peierls compounds

# 3.3 Phase transitions

At high temperatures, the temperature dependence of the magnetic susceptibility  $\chi$  of TiOCl (TiOBr) can be described by the one-dimensional Heisenberg model [75]. After substraction of the Curie tail, which accounts for paramagnetic impurities, the high temperature part of  $\chi(T)$  (above 130 K) in TiOCl can be fitted to the Bonner-Fisher-curve with a next-neighbor exchange constant J = 660 K [26].<sup>2</sup>

In TiOBr the Bonner-Fisher-curve does not provide a good fit for  $\chi(T)$  [76], leading to a far too small value for the next-neighbor exchange J = 188 K [74], compared to J = 375 K as estimated by Rückamp *et al.* [9].

<sup>&</sup>lt;sup>2</sup>Kataev *et al.* fitted the Bonner-Fisher-curve with J = 676 K [25]



Fig. 3.4: (a) Magnetic susceptibility of TiOCl fitted to the Bonner-Fisher-curve. The inset shows a hysteresis indicating a first order phase transition at  $T_{c1}$ . (b) Magnetic susceptibility of TiOBr fitted to the Bonner-Fisher-curve. (Figures taken from Refs. [26], [8] and [74])

In both compounds, there is a kink in  $\chi(T)$  at  $T_{c2} = 91$  K (48 K) followed by a sharp drop at  $T_{c1}$ , where the susceptibility suddenly vanishes (see Fig. 3.4). These observations were confirmed by electron-spin-resonance (ESR) measurements of the spin susceptibility [25].

An observed hysteresis at  $T_{c1}$  (see inset in Fig. 3.4a) indicates the first-order character of the low temperature phase transition [8], which is not expected in a conventional spin-Peierls scenario, where a second order phase transition separates the paramagnetic ground state from the dimerized non-magnetic phase [7].

Recently, Abel *et al.* [64] suggested that it is actually the structural transition to the incommensurate (nearly dimerized) state at  $T_{c2}$ , which defines the spin-Peierls transition.

This transition is of second order and it is supposed to be driven by a softening of a longitudinal acoustic phonon at the zone boundary, which has already been predicted to appear in conventional spin-Peierls compounds from Cross and Fisher [38].

Actually, it is the first time such an soft phonon has been observed suggesting that the titanium oxyhalogenides, in contrast to CuGeO<sub>3</sub> [77, 78], may fall within the "adiabatic" regime, i.e. where phonon energies are small compared to the magnetic interactions.

Other quantities, such as the linear thermal expansion  $\alpha$  and the specific heat  $C_p$ , as well show the existence of two distinct phase transitions (see Fig. 3.5) [9].



Fig. 3.5: Thermal expansion  $\alpha = \partial L / \partial T$  and specific heat  $C_p$  of TiOCl (l.h.s.) and TiOBr (r.h.s). (Figure taken from Ref. [9])

#### 3.4 Commensurate and incommensurate phase



Fig. 3.6: Superlattice reflections displaced from the fundamental Bragg peaks (h, k, l) by the modulation wave vector  $\vec{q} = (\pm q_1, \frac{1}{2} \pm \delta, 0)$ .

(a) *q* scan along b-direction centered at (2, 1.5, -1). A single peak at position  $(h, k + \frac{1}{2}, l)$  at T = 63 K indicates a doubling of the unit cell along b-direction and corresponds to the commensurate modulation wave vector  $\vec{q} = (0, \frac{1}{2}, 0)$ , while the two peaks appearing at T = 67 K correspond to an incommensurate modulation in b-direction with  $\vec{q} = (0, \frac{1}{2} \pm \delta, 0)$ . (b) *q* scan along a-direction centered at (-2, -1.5, -1). While the single peak at T = 66 K indicates again a twofold superstructure with  $q_1 = 0$  and  $\delta = 0$ , the two peaks at positions  $(-2 \pm q_1, -1.5, -1)$  correspond to an incommensurate modulation in a-direction with  $\vec{q} = (\pm q_1, \frac{1}{2}, 0)$ . (Figures taken from Refs. [79] and [80])

The dimerization of the Ti ions at low temperatures was established by X-ray diffraction measurements, where a doubling of the unit cell along the b-direction has been observed [79, 81]. This is indicated by a superlattice reflection peak appearing below  $T_{c1}$  at positions displaced from the fundamental Bragg peaks by a commensurate modulation wave vector  $\mathbf{q} = (0, \frac{1}{2}, 0)$  (see Fig. 3.6a).

In the intermediate phase  $T_{c1} < T < T_{c2}$ , two peaks appear, which correspond to incommensurate superlattice reflections with a modulation wave vector  $\mathbf{q} = (\pm q_1, \frac{1}{2} \pm \delta, 0)$  [80] (see Fig. 3.6b).

The parameter  $\delta$  describes the incommensurability along the chains in b-direction, while  $q_1$  describes the incommensurability perpendicular to the chains in a-direction. The incommensurabilities increase with increasing temperature. The temperature dependence of the incommensurability along the chains is almost linear [80] (see Fig. 3.7).



Fig. 3.7: Temperature dependence of the incommensurabilities along ( $\delta$ ) and perpendicular ( $q_1$ ) to the chains. (Figure taken from Ref. [80])

The origin of the incommensurability  $\delta$  along the chains can be explained within a scenario proposed by Rückamp *et al.* [9]. Accordingly, the energy to form a soliton can be gained from the frustrated elastic coupling between the Ti chains. In a Ginzburg-Landau expansion of the free energy in the displacements parallel to the chains, this frustration leads to terms which favor a minimum corresponding to an incommensurate modulation. In Subsection 3.5 this scenario will be discussed in detail.

However, the origin of the incommensurate modulation perpendicular to the chains is not explained within this model. Rückamp *et al.* [9] proposed that a component of the displacement in a-direction could yield an incommensurate value for  $q_1$ . While finite values of the displacement component along c-direction have been observed in the distorted low-temperature phase [79], Schönleber *et al.* [80] measured very small nonzero amplitudes along the a-direction in the intermediate phase, which can hardly act as driving force for the observed incommensurability along a.

The displacement of the Ti ions within the ac-plane is combined with a displacement of O and Cl/Br ions within the bc-plane. Thereby the displacements of O and Cl/Br ions just follow the Ti displacements indicated by equal distances between these atoms in order to minimize the internal strain of the superstructure [79] (see Fig. 3.8).



Fig. 3.8: Displacements in the twofold spin-Peierls state. (Figure taken from Ref. [80])

The nature of the incommensurate phase between  $T_{c1}$  and  $T_{c2}$  was reported to be an incommensurate modulation of the twofold superstructure in the dimerized phase. Minimum and maximum values of the bond distances and bond angles in the incommensurate phase are equal to the corresponding values in the commensurate phase. Furthermore, the amplitude of the incommensurate modulation of the displacements is of similar size as the displacements in the commensurate phase [80].

# 3.5 Interchain frustration as an explanation for the incommensurability along the chains

While in conventional spin-Peierls systems the solitonic excitation gap can be overcome by applying a magnetic field, in the titanium oxyhalogenides solitons and incommensurate modulations are already present in absence of a magnetic field.

Rückamp *et al.* [9] proposed that the energy to form a soliton is gained from the frustrated elastic coupling between the Ti chains. In a Ginzburg-Landau expansion of the free energy this frustration leads to terms which favor a minimum corresponding to an incommensurate modulation. The system has to become incommensurate in order to gain any energy from the interchain coupling. This scenario implies that the spin-Peierls mechanism is the driving force for both phase transitions.



Fig. 3.9: Two-dimensional modell of a system of frustrated Ti spin chains.

In terms of the displacement  $\Phi_{n,m}$  of the Ti ions along the b-direction, where *n* indicates the different chains along the a-direction and *m* the sites within the chains along b-direction, the free energy in Ginzburg-Landau expansion up to second order in the displacements has the following form

$$\Delta F_{2D} = \underbrace{\frac{a_0}{2} \sum_{n,m} (\Phi_{n,m})^2}_{F_{2D,II}} + \underbrace{\frac{a_1}{2} \sum_{n,m} \Phi_{n,m} \Phi_{n,m-1}}_{F_{2D,II}} + \underbrace{\frac{b}{2} \sum_{n,m} \Phi_{n,m} (\Phi_{n+1,m} + \Phi_{n+1,m-1})}_{F_{2D,III}} . \quad (3.1)$$

The term  $F_{2D,II}$  describes the tendency toward a spin-Peierls distortion ( $a_1 > 0$ ). In case of perfect dimerization, neighboring Ti ions displace with the same amplitude, but alternating sign, and the term  $F_{2D,II}$  becomes negative, while the term  $F_{2D,III}$  vanishes.

The tendency of a spin chain to dimerize increases on decreasing temperature because the entropic effects are reduced. This leads to increasing values of the magneto-elastic coupling  $a_1$ .

In Fourier space the free energy can be written as

$$\Delta F_{2D} = \frac{1}{2} \sum_{h,k} \omega_{h,k} |\Phi_{h,k}|^2 .$$
(3.2)

In order to calculate the dispersion  $\omega_{h,k}$ , we use the following Fourier transformation

$$\Phi_{n,m} = \frac{1}{N} \sum_{h,k} e^{i\vec{k}\vec{r}_{n,m}} \Phi_{h,k} \qquad \qquad \vec{k} = \begin{pmatrix} h\\ k \end{pmatrix}, \quad \vec{r}_{n,m} = \begin{pmatrix} \frac{1}{2}n\\ m + \frac{1}{2}n \end{pmatrix} a \tag{3.3}$$

$$\stackrel{a=1}{=} \frac{1}{N} \sum_{h,k} e^{ikm} e^{i(h+k)\frac{1}{2}n} \Phi_{h,k}$$
(3.4)

with a modulation wave vector  $\vec{k}$  containing components perpendicular (*h*) and parallel (*k*) to the chains , the position vectors  $\vec{r}_{n,m}$  and a lattice spacing a = 1.

We obtain the following contributions to the free energy in Fourier space

$$F_{2D,I} = \frac{a_0}{2N^2} \sum_{n,m} \sum_{\substack{h,h'\\k,k'}} e^{i(k+k')m} e^{i(h+h'+k+k')\frac{1}{2}n} \Phi_{h,k} \Phi_{h',k'}$$
  
$$= \frac{a_0}{2N^2} \sum_{\substack{h,h'\\k,k'}} N\delta_{k',-k} N\delta_{h',-h} \Phi_{h,k} \Phi_{h',k'}$$
  
$$= \frac{a_0}{2} \sum_{\substack{h,k}} \Phi_{h,k} \Phi_{-h,-k}$$
  
$$= \frac{a_0}{2} \sum_{\substack{h,k}} |\Phi_{h,k}|^2 , \qquad (3.5)$$

$$F_{2D,II} = \frac{a_1}{2N^2} \sum_{n,m} \sum_{\substack{h,h'\\k,k'}} e^{i(k+k')m} e^{-ik'} e^{i(h+h'+k+k')\frac{1}{2}n} \Phi_{h,k} \Phi_{h',k'}$$
  
$$= \frac{a_1}{2} \sum_{\substack{h,k}} e^{ik} |\Phi_{h,k}|^2$$
  
$$= \frac{a_1}{2} \sum_{\substack{h,k}} \frac{1}{2} (e^{ik} + e^{-ik}) |\Phi_{h,k}|^2$$
  
$$= \frac{a_1}{2} \sum_{\substack{h,k}} \cos(k) |\Phi_{h,k}|^2 , \qquad (3.6)$$

$$F_{2D,III} = \frac{b}{2N^2} \sum_{\substack{n,m \ h,h' \\ k,k'}} e^{i(k+k')m} e^{i(h+h'+k+k')\frac{1}{2}n} \left(e^{i\frac{(h'+k')}{2}} + e^{-ik+i\frac{(h'+k')}{2}}\right) \Phi_{h,k} \Phi_{h',k'}$$
$$= \frac{b}{2} \sum_{\substack{h,k \ h}} e^{-i\frac{h}{2}} \left(e^{-i\frac{k}{2}} + e^{i\frac{k}{2}}\right) |\Phi_{h,k}|^2$$
$$= \frac{b}{2} \sum_{\substack{h,k \ h}} 2\cos\left(\frac{h}{2}\right) \cos\left(\frac{k}{2}\right) |\Phi_{h,k}|^2 .$$
(3.7)

Altogether, the following expression for the free energy in Fourier space results

$$\Delta F_{2D} = \frac{1}{2} \sum_{h,k} \omega_{h,k} |\Phi_{h,k}|^2$$
(3.8)

with 
$$\omega_{h,k} = a_0 + a_1 \cos\left(k\right) + 2b \cos\left(\frac{h}{2}\right) \cos\left(\frac{k}{2}\right)$$
. (3.9)

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As mentioned before, the magneto-elastic intrachain coupling  $a_1$  increases with decreasing temperature. For vanishing interlayer coupling *b* the system undergoes a spontaneous dimerization at  $k = \pi$ , as soon as the temperature is small enough to assure that  $a_0 - a_1 < 0$ .

In order to minimize  $\Delta F_{2D}$  for non-vanishing intrachain coupling *b*, we have a look at the partial derivatives

$$\frac{\partial \Delta F_{2D}}{\partial h} \stackrel{!}{=} 0$$

$$\Leftrightarrow 0 = -\sin\left(\frac{h}{2}\right)\cos\left(\frac{k}{2}\right)$$
(3.10)

and

$$\frac{\partial \Delta F_{2D}}{\partial k} \stackrel{!}{=} 0$$

$$\Leftrightarrow 0 = -a_1 \sin\left(k\right) - b \cos\left(\frac{h}{2}\right) \sin\left(\frac{k}{2}\right)$$

$$\Leftrightarrow 0 = -2a_1 \sin\left(\frac{k}{2}\right) \cos\left(\frac{k}{2}\right) - b \cos\left(\frac{h}{2}\right) \sin\left(\frac{k}{2}\right)$$

$$\Leftrightarrow 0 = -2a_1 \cos\left(\frac{k}{2}\right) - b \cos\left(\frac{h}{2}\right). \qquad (3.11)$$

The free energy is minimized for

$$h_{\min} = 0 \tag{3.12}$$

$$k_{\min, 2D} = 2 \arccos\left(\frac{-b}{2a_1}\right) \approx \pi + \frac{b}{a_1}$$
 (3.13)

We see that the system becomes incommensurate for any finite value of the elastic interchain coupling *b*. For a commensurate modulation with  $k = \pi$ , the *b*-term vanishes in (3.9). Therefore, the system has to become incommensurate in order to gain energy from the coupling.

The incommensurabilities in a- and b-direction are defined as the differences between incommensurate and commensurate modulation components

$$q_1 = h_{\min} \tag{3.14}$$

$$\delta_{2\mathrm{D}} = k_{\min, 2\mathrm{D}} - \pi \approx \frac{b}{a_1} \,. \tag{3.15}$$

We see that the modulation wave vector, which minimizes the free energy in second order expansion, will always be incommensurate, i.e.,  $\delta_{2D}$  will always be finite, for a finite

interchain coupling *b*. Therefore, the lock-in transition to the dimerized commensurably modulated ground state is not described in this order.

Furthermore, infinite amplitudes of the displacements would be favored in the second order expansion of the free energy. Therefore, this order does not suffice for the description and the free energy has to be expanded up to fourth order.

# 4 Description of the incommensurate phase and the phase transition to the commensurate phase in a simplified one-dimensional model

The aim of the present thesis is to understand the mechanism, which leads to the incommensurate phase in the titanium oxyhalogenides at intermediate temperatures and drives the phase transition to the commensurate low-temperature phase.

In order to capture the incommensurate-commensurate phase transition within the model of Rückamp *et al.* [9], presented in the previous subsection, the Ginzburg-Landau expansion of the free energy will be expanded up to fourth order. The minimization is carried out numerically.

The temperature dependence of the incommensurability along the chains will be discussed and compared with the experimental data in Reference [80].

However, because our main aim is to understand the physics leading to the observed data, this work concentrates on the discussion of a system of two frustrated spin chains, although it makes the reproduction of experimental data more difficult. The advantage of such a one-dimensional model, in which only a modulation along the chain direction is investigated, is that the analysis of the system is easier and the results are more accessible and easier to understand than in the two-dimensional case.

In the following section, the one-dimensional model is presented, followed by a short description of the structure of the implemented program in Subsection 4.1.1. Subsequently, some preparatory calculations, as well as a parameter analysis, are presented in Subsections 4.1.2 to 4.1.4. Since some considerations can only be explained with regard to the programming details, these are included within the subsections. The same applies to several results.

Finally, in Section 4.2 the obtained results are presented and discussed in detail.

We note that we refer to the phase transition from the incommensurate to the commensurate phase as lock-in transition. However, this designation should not suggest a first order character of the phase transition.

# 4.1 Simplified one-dimensional model for the description of the incommensurate phase and the lock-in transition

In order to describe the lock-in transition to the commensurate phase, the free energy is now expanded up to quartic order in the displacements

$$\Delta F = \frac{a_0}{2} \sum_{n,m} (\Phi_{n,m})^2 + \frac{a_1}{2} \sum_{n,m} \Phi_{n,m} \Phi_{n,m-1} + \frac{b}{2} \sum_{n,m} \Phi_{n,m} (\Phi_{n+1,m} + \Phi_{n+1,m-1}) + \frac{1}{4} \sum_{n,m} (\Phi_{n,m})^4 .$$
(4.1)

Without loss of generality, we chose the prefactor of the quartic term and therewith the energy scale to be equal to unity. Since the Fourier transformation of  $\Delta F$  is not trivial anymore, a program is implemented in order to minimize the free energy numerically.

To obtain a better understanding of how the gained solutions describe the physics, the calculations are done for the one-dimensional case, where a system of two frustrated spin chains is investigated and where a modulation only in b-direction occurs.

Due to the shifts between the chains, the system can be simplified to a single spin chain with a frustrated nearest neighbor coupling b and a next nearest neighbor coupling  $a_1$ .<sup>1</sup>



Fig. 4.1: Simplification of two frustrated spin chains with inter- and intrachain coupling to a single spin chain with nearest neighbor and next nearest neighbor coupling.

The free energy for a single chain with such properties has the following form in position space

$$\Delta F = \frac{a_0}{2} \sum_i \Phi_i^2 + \frac{a_1}{2} \sum_i \Phi_i \Phi_{i-2} + \frac{b}{2} \sum_i \Phi_i \Phi_{i-1} + \frac{1}{4} \sum_i \Phi_i^4 .$$
(4.2)

Since we do not want to confuse the reader with inconsistent terms for the important parameters, we will anticipate one of our results as this point: We found that the parameter  $a_0$  has only a rescaling effect on the quantities in which we are interested in (see Section 4.2.2).

In order to check the influence of the parameter  $a_0$ , we rescale the displacements as followed

 $\Phi 
ightarrow ilde{\Phi} = \lambda \Phi$  ,

<sup>&</sup>lt;sup>1</sup>Nevertheless, we still refer to b and  $a_1$  as inter- and intrachain coupling.
and analyze the resulting effect on the free energy (4.2)

$$\Delta \tilde{F} = \frac{a_0}{2} \lambda^2 \sum_i \Phi_i^2 + \frac{a_1}{2} \lambda^2 \sum_i \Phi_i \Phi_{i-2} + \frac{b}{2} \lambda^2 \sum_i \Phi_i \Phi_{i-1} + \frac{1}{4} \lambda^4 \sum_i \Phi_i^4.$$

Choosing  $\lambda = \sqrt{a_0}$ , we can write the free energy in terms of the parameters  $\gamma = a_1/a_0$ and  $\beta = b/a_0$ 

$$rac{\Delta ilde{F}}{a_0^2} = rac{1}{2} \sum_i \Phi_i^2 + rac{\gamma}{2} \sum_i \Phi_i \Phi_{i-2} + rac{eta}{2} \sum_i \Phi_i \Phi_{i-1} + rac{1}{4} \sum_i \Phi_i^4 \ .$$

The rescaled couplings  $\gamma$  and  $\beta$  are the two remaining independent parameters, while the parameter  $a_0$  simply rescales the absolute value of the free energy  $\Delta F$  and the value of the displacements. Since we are not interested in the absolute values of  $\Delta F$ , we can choose  $a_0 = 1$  without loss of generality.<sup>2</sup>

Therefore, we analyze the following free energy in position space

$$\Delta F = \frac{1}{2} \sum_{i} \Phi_{i}^{2} + \frac{\gamma}{2} \sum_{i} \Phi_{i} \Phi_{i-2} + \frac{\beta}{2} \sum_{i} \Phi_{i} \Phi_{i-1} + \frac{1}{4} \sum_{i} \Phi_{i}^{4} .$$
(4.3)

## 4.1.1 Structure of the implemented program

We can use the Polak-Ribiere variant of conjugate gradient algorithm for the minimization of the free energy in Ginzburg-Landau expansion up to fourth order because it is possible to calculate the derivatives of the free energy.

The algorithm requires good guesses for the initial vectors because the solutions depend strongly on them. This dependence on the initial vectors is quite easy to understand if we remember that domain walls are created in the incommensurate phase. In most cases, the algorithm is not able to change the number of domain walls predefined by the initial vector and is therefore stuck in such a local minimum.

Therefore, we try different initial vectors, compare the free energy of the solutions and choose the one with the lowest energy  $\Delta F$  as the true minimum.

In order to determine the wave vector of this modulation, we apply a Fast Fourier Transformation. The incommensurability  $\delta$  can be calculated as the difference between this modulation wave vector and the modulation wave vector in the commensurate case.

All calculations are realized for various coupling constants. The interchain coupling  $\beta$  is increased from the value  $\beta = 0.1727127512$ , which has to be chosen if experimental data shall be reproduced and which is calculated in Section 4.1.4.3, with a step size of  $\Delta\beta = 0.02$  till  $\beta \le 0.4327127512$ .

<sup>&</sup>lt;sup>2</sup>In Subsection 4.2.4 we compare the values of the formation energy of a soliton for various intrachain couplings  $\gamma$ . However, we are mainly interested in the change of sign of the formation energies. Therefore, there is no conflict in using the rescaled values of  $\Delta F$ .

Within each  $\beta$ -loop the intrachain coupling  $\gamma$  is increased from its onset value  $\gamma_c$ , which corresponds to the onset of the incommensurate phase and which is calculated in Section 4.1.4.1, with a step size of  $\Delta \gamma = \beta^2 / 500$  till  $\gamma \leq (\gamma_c + \beta^2)$ .<sup>3</sup>

## 4.1.2 Optimal initial vectors

We assume that the solution for the modulation of the displacements does not differ much from the one, which minimizes the free energy in second order expansion. Therefore, we calculate the modulation of the displacements in second order expansion, for the simplified one-dimensional model with the free energy

$$\Delta F = \underbrace{\frac{1}{2} \sum_{i} \Phi_{i}^{2}}_{F_{\mathrm{I}}} + \underbrace{\frac{\gamma}{2} \sum_{i} \Phi_{i} \Phi_{i-2}}_{F_{\mathrm{II}}} + \underbrace{\frac{\beta}{2} \sum_{i} \Phi_{i} \Phi_{i-1}}_{F_{\mathrm{III}}}$$
(4.4)

The free energy in Fourier space looks slightly different from the one before

$$\Delta F = \frac{1}{2} \sum_{k} \omega_k |\Phi_k|^2 \tag{4.5}$$

with 
$$\omega_k = 1 + \gamma \cos(2k) + \beta \cos(k)$$
 (4.6)

and it is minimized by the modulation wave vector

$$k_{\min} = \arccos\left(\frac{-\beta}{4\gamma}\right) \approx \frac{\pi}{2} + \frac{\beta}{4\gamma}.$$
 (4.7)

Since the unit cell has doubled compared to the unit cell in the two-dimensional model, the modulation wave vector should have halved compared to the modulation wave vector  $k_{\min, 2D}$ . This is the case for the commensurate phase, where the displacement is now modulated by the modulation wave vector  $k_{\min} = \pi/2$  in contrast to  $k_{\min, 2D} = \pi$  in the two-dimensional model.

However, if we compare (4.7) to  $k_{\min, 2D} = 2 \arccos(-\beta/2\gamma) \approx \pi + \beta/\gamma$  (3.13)<sup>4</sup>, the relation  $k_{\min, 2D} = 2k_{\min}$  is not valid in the incommensurate case. The reason for that is that in term  $F_{2D,\text{III}}$  in (3.1) the interchain interactions are counted double, while they are counted simply in term  $F_{\text{III}}$  in (4.4). Introducing an additional factor 1/2 in  $F_{2D,\text{III}}$  in (3.1) would lead to  $k_{\min, 2D} = 2k_{\min}$ .

<sup>&</sup>lt;sup>3</sup>In fact the  $\gamma$ -loop starts from the initial value  $\gamma = (\gamma_c + \beta^2/30)$  slightly above the onset because the algorithm is not able to find a minimum for  $\gamma = \gamma_c$  (see Subsection 4.1.4.1). The initial value, the step size and the final value of  $\gamma$  were determined by trial and error, so that a good resolution for the intrachain coupling dependence of the incommensurability  $\delta$  for each  $\beta$ -value was obtained.

<sup>&</sup>lt;sup>4</sup>We replaced *b* and  $a_1$  in (3.13) with  $\beta$  and  $\gamma$ .

# 4.1 Simplified one-dimensional model for the description of the incommensurate phase and the lock-in transition

The modulation of the displacements, which minimizes the free energy (4.4), acquires the following form

$$\Phi_i = a \cos\left(k_{\min} \cdot i + \frac{\pi}{4}\right). \tag{4.8}$$

The additional phase shift of  $\pi/4$  assures that the displacements in the commensurate phase all have the same amplitude (see Fig. 4.2).<sup>5</sup>

<sup>&</sup>lt;sup>5</sup>By amplitude of the displacements we mean the amount by which the Ti ions are displaced from their original positions, while we refer to *a* as the modulation amplitude.



Initial vector without phase shift  $\Phi$  [i]= a\*cos( $\pi/2^*$ i)





Fig. 4.2: (a) Without a phase shift, the displacement in the commensurate phase vanishes on the odd sites (red dots). (b) Adding a phase shift of  $\pi/4$  assures that all Ti atoms displace with the same amplitude, pairwise in the same direction (green bars highlight positive amplitudes while yellow bars highlight negative amplitudes).

# 4.1 Simplified one-dimensional model for the description of the incommensurate phase and the lock-in transition

In order to calculate the optimal amplitude for the initial vectors, we calculate the free energy in dependence of the modulation amplitude a. Therefore, we insert the displacements (4.8) into the free energy (4.3) in fourth order expansion

$$\Delta F = \underbrace{\frac{1}{2} \sum_{i} \Phi_{i}^{2}}_{F_{\mathrm{I}}} + \underbrace{\frac{\gamma}{2} \sum_{i} \Phi_{i} \Phi_{i-2}}_{F_{\mathrm{II}}} + \underbrace{\frac{\beta}{2} \sum_{i} \Phi_{i} \Phi_{i-1}}_{F_{\mathrm{III}}} + \underbrace{\frac{1}{4} \sum_{i} \Phi_{i}^{4}}_{F_{\mathrm{IV}}}.$$

Using

$$\cos^{2}(x) = \frac{1}{2} + \frac{1}{2}\cos(2x)$$
(4.9a)

$$\cos(x \pm y) = \cos(x)\cos(y) \mp \sin(x)\sin(y)$$
(4.9b)

$$\cos(x)\sin(x) = \frac{1}{2}\sin(2x)$$
 (4.9c)

$$\cos^{4}(x) = \frac{3}{8} + \frac{1}{2}\cos(2x) + \frac{1}{8}\cos(4x)$$
(4.9d)

yields the following expressions

$$\begin{split} F_{\rm I} &= \frac{1}{2} a^2 \sum_i \cos^2 \left( k_{\rm min} \cdot i + \frac{\pi}{4} \right) \\ &= \frac{1}{2} a^2 \sum_i \left[ \frac{1}{2} + \frac{1}{2} \cos \left( 2k_{\rm min} \cdot i + \frac{\pi}{2} \right) \right] \\ &= \frac{1}{2} a^2 \left[ \frac{N}{2} - \frac{1}{2} \sum_i \underbrace{\sin \left( 2k_{\rm min} \cdot i \right)}_{i=0 \text{ for } k_{\rm min} \neq \frac{\pi}{2}} \right] \\ &= \frac{1}{2} a^2 \left[ \frac{N}{2} - \frac{1}{2} \sum_i \underbrace{\sin \left( 2k_{\rm min} \cdot i \right)}_{i=0 \text{ for } k_{\rm min} \neq \frac{\pi}{2}} \right] \\ &= \frac{N}{4} a^2 \,, \\ F_{\rm II} &= \frac{\gamma}{2} a^2 \sum_i \cos \left( k_{\rm min} \cdot i + \frac{\pi}{4} \right) \cos \left( k_{\rm min} \cdot i + \frac{\pi}{4} - 2k_{\rm min} \right) \\ &\frac{49b}{2} \frac{\gamma}{2} a^2 \sum_i \left[ \cos^2 \left( k_{\rm min} \cdot i + \frac{\pi}{4} \right) \cos \left( 2k_{\rm min} \right) + \cos \left( k_{\rm min} \cdot i + \frac{\pi}{4} \right) \sin \left( k_{\rm min} \cdot i + \frac{\pi}{4} \right) \sin \left( 2k_{\rm min} \right) \right] \\ &= \frac{\gamma}{2} a^2 \left[ \frac{N}{2} \cos \left( 2k_{\rm min} \right) + \sum_i \frac{1}{2} \sin \left( 2k_{\rm min} \cdot i + \frac{\pi}{2} \right) \sin \left( 2k_{\rm min} \right) \right] \\ &= \frac{\gamma}{2} a^2 \left[ \frac{N}{2} \cos \left( 2k_{\rm min} \right) + \frac{1}{2} \sum_i \cos \left( 2k_{\rm min} \cdot i \right) \underbrace{\sin \left( 2k_{\rm min} \right)}_{i=0 \text{ for } k_{\rm min} \neq \frac{\pi}{2}} \right] \\ &= \frac{N}{4} \gamma \cos \left( 2k_{\rm min} \right) a^2 \,, \end{split}$$

$$egin{split} F_{\mathrm{III}} &= rac{eta}{2} a^2 \sum_i \cos\left(k_{\mathrm{min}} \cdot i + rac{\pi}{4}
ight) \cos\left(k_{\mathrm{min}} \cdot i + rac{\pi}{4} - k_{\mathrm{min}}
ight) \ &= rac{N}{4} eta \cos\left(k_{\mathrm{min}}
ight) a^2 \,, \end{split}$$

$$F_{\rm IV} = \frac{a^4}{4} \sum_i \cos^4 \left( k_{\rm min} \cdot i + \frac{\pi}{4} \right)$$

$$\stackrel{4.9d}{=} \frac{a^4}{4} \sum_i \left[ \frac{3}{8} + \frac{1}{2} \cos \left( 2k_{\rm min} \cdot i + \frac{\pi}{2} \right) + \frac{1}{8} \cos \left( 4k_{\rm min} \cdot i + \pi \right) \right]$$

$$= \frac{a^4}{4} \left[ \frac{3N}{8} - \sum_i \left[ \frac{1}{2} \underbrace{\sin \left( 2k_{\rm min} \cdot i \right)}_{=0 \text{ for } k_{\rm min} = \frac{\pi}{2}} + \frac{1}{8} \underbrace{\cos \left( 4k_{\rm min} \cdot i \right)}_{=1 \text{ for } k_{\rm min} = \frac{\pi}{2}} \right] \right]$$

$$= \begin{cases} \frac{N}{4} \frac{1}{4} a^4 & \text{for } k_{\rm min} = \frac{\pi}{2} \\ \frac{N}{4} \frac{3}{8} a^4 & \text{for } k_{\rm min} \neq \frac{\pi}{2} \end{cases}.$$

In terms of the dispersion  $\omega_{k_{\min}} = 1 + \gamma \cos(2k_{\min}) + \beta \cos(k_{\min})$  the free energy can be written as

$$\Delta F_{\text{com}} = \frac{N}{4} \left[ \omega_{k_{\min}} a^2 + \frac{1}{4} a^4 \right] \qquad \text{for } k_{\min} = \frac{\pi}{2} \qquad (4.10a)$$

$$\Delta F_{\rm incom} = \frac{N}{4} \left[ \omega_{k_{\rm min}} a^2 + \frac{3}{8} a^4 \right] \qquad \qquad \text{for } k_{\rm min} \neq \frac{\pi}{2} . \tag{4.10b}$$

The amplitude which minimizes  $\Delta F$  can be calculated from  $\frac{\partial \Delta F}{\partial a} = 0$ . For  $a \neq 0$ , the optimal initial vector amplitude is given by

$$a_{\rm com} = \pm \sqrt{-2\omega_{k_{\rm min}}} \qquad \qquad \text{for } k_{\rm min} = \frac{\pi}{2} \qquad (4.11a)$$

$$a_{\rm incom} = \pm \sqrt{-\frac{4}{3}} \omega_{k_{\rm min}}$$
 for  $k_{\rm min} \neq \frac{\pi}{2}$  (4.11b)

The Ti ions only displace if they gain energy from the displacement, i.e., if  $\Delta F < 0$ . This is the case, if the dispersion  $\omega_{k_{\min}}$  becomes negative. Accordingly the amplitudes are real valued.

### **Programming details:**

The initial vectors are implemented as

$$p[i] = a \cdot \cos(k \cdot i) \text{ with } k = \frac{2\pi n}{N}.$$
(4.12)

The system has a size of N = 2048 sites, i.e., N/2 = 1024 sites per chain. The modulation parameter *n* allows to change the modulation wave vectors. Since the commensurate phase corresponds to  $k = \pi/2$ , the modulation parameter in the commensurate phase is n = N/4 = 512. For n = 512, the commensurate amplitude  $a_{\text{com}}$  is inserted for the parameter *a* in (4.12). For incommensurate values  $n \neq 512$  of the modulation parameter, the incommensurate amplitude  $a_{\text{incom}}$  is inserted.

In order to find the true minimum, we try different initial vectors, compare the free energy of the solutions and choose the one with the lowest energy  $\Delta F$  as the true minimum (see Fig. 4.3). This solution is saved in the data vector  $p_{min}[i]$ . The modulation parameter n which realizes the corresponding initial vector is saved in the variable  $n_{min}$ .

In Figure 4.3 we see that the energy  $\Delta F$  of the solution and the energy  $\Delta F$  of the initial vector are the same for the commensurate initial modulation parameter n = 512, i.e., the minimization algorithm is not able to create domain walls when the initial vector itself does not have any domain walls.

In Figures 4.3a-c we also see that the minimization algorithm is not able to increase the number of domain walls predefined by the initial vectors. However, for some reason, there are a few exceptions where the algorithm is suddenly able to create additional domain walls in the solutions (see outliers indicated by black points in Figs. 4.3a and b).

In Figures 4.3d and 4.3e we can see that close to the transition to the commensurate phase, commensurate and incommensurate local minima have almost the same size (the energy differences are of the order  $10^{-6}$ ). Moreover, the minimization algorithm finds the true minimum of  $\Delta F$  for a broader range of initial vectors. The reason for that could be, that the algorithm has less problems to decrease the number of domain walls predefined by the initial vectors.

In Figure 4.4 a higher resolution of the dependence of the energy of the solutions just before the lock-in, i.e., for the largest  $\gamma$ -value for which an incommensurate  $n_{min}$  can be observed, is displayed for various values of the interchain coupling  $\beta$ .



Fig. 4.3: Dependence of the free energy per site on the modulation parameter *n*, which realizes different initial vectors, for various values of the intrachain coupling  $\gamma$  (a)-(d) in the incommensurate and (e)-(f) in the commensurate phase.



Fig. 4.4: Dependence of the minimized free energy per site on the modulation parameter n, which realizes different initial vectors, for various values of the interchain coupling  $\beta$ . Only the curves for the respective  $\gamma$  values just before the lock-in in the incommensurate phase are displayed. The *n*-values in the legend identify the energy minimum, which cannot be identified by the naked eye as the energy differences are partly of the order  $10^{-7}$ .

In Subsection 4.2.4 we calculate the formation energy of a soliton (kink). Therefore, although there is no case where this solution is the true minimum, we need the solution with the smallest possible incommensurability, hence, with the smallest number of kinks. This is the solution for n = N/4 + 1 = 513. Although we will see in Subsection 4.2.4.1 that due to periodic boundary conditions at least two kinks per chain are created, we call the solution for n = 513 from here on 1-kink-solution.<sup>6</sup>

As mentioned in the introduction in Section 2.4.2, the modulation for a small number of solitons is more kinklike than sinusoidal. Therefore, we consider box-shaped initial vectors for the case n = 513.

For the kink solution we consider the following box-shaped modulation as initial vector for the displacements

$$\Phi_i = a_{\text{kink}} \cdot \text{sign}\left[\cos\left(\frac{2\pi \cdot 513}{N} \cdot i + \frac{\pi}{4}\right)\right].$$
(4.13)

In order to calculate the optimal amplitude  $a_{kink}$ , we insert (4.13) into the free energy (4.3). Maple13 calculates the following free energy in dependence of the modulation amplitude

$$\Delta F(n = 513) = \frac{N}{2} \left[ \left( 1 - \left( 1 - \frac{8}{N} \right) \gamma - \frac{4}{N} \beta \right) a_{\text{kink}}^2 + \frac{1}{2} a_{\text{kink}}^4 \right] .$$
(4.14)

The amplitude which minimizes  $\Delta F(n = 513)$  can be calculated from  $\frac{\partial \Delta F(n=513)}{\partial a_{kink}} = 0$ . For  $a_{kink} \neq 0$ , the optimal initial vector amplitude is given by

$$a_{\rm kink} = \pm \sqrt{-\left(1 - \left(1 - \frac{8}{N}\right)\gamma - \frac{4}{N}\beta\right)}.$$
(4.15)

## 4.1.3 Calculation of the incommensurability $\delta$

As in the two-dimensional model, the incommensurability  $\delta_{1D}$  along the chains can be calculated as the difference between the modulation wave vector of a solution and the modulation wave vector in the commensurate phase  ${}^7 k_{\min} = \pi/2$ 

$$\delta_{1D} = k_{\min} - \frac{\pi}{2} = \arccos\left(\frac{-\beta}{4\gamma}\right) - \frac{\pi}{2}.$$
(4.16)

<sup>&</sup>lt;sup>6</sup>Due to periodic boundary conditions, the smallest number of kinks which can be realized in the solutions is four (see "Programming details" in Section 4.2.4.1).

<sup>&</sup>lt;sup>7</sup>Introducing an additional factor 1/2 in  $F_{2D,III}$  in (3.1) would lead to  $\delta_{2D} = 2\delta_{1D}$  (see Section 4.1.2).

# 4.1 Simplified one-dimensional model for the description of the incommensurate phase and the lock-in transition

We want to compare the numerically determined values of  $\delta_{1D}$  with experimental data, where the modulation wave vector  $\vec{q}$  is measured in reciprocal lattice units  $\begin{bmatrix} 2\pi \\ a \end{bmatrix}$  and where the Ti ions are displaced by the modulation wave vector  $\vec{q} = (0, \frac{1}{2}, 0)$  in the commensurate phase (see Section 3.4).

Taking into account the doubled unit cell and assuming a lattice spacing a = 1, we can rewrite the modulation wave vector  $k_{\min}$  and the incommensurability  $\delta_{1D}$  in terms of the reciprocal lattice units  $[\pi]$ .

In order to distinguish the two notations, we refer to the modulation wave vector component along the chains and to the incommensurability in terms of the reciprocal lattice units as q and  $\delta$ , while  $k_{\min}$  and  $\delta_{1D}$  denote the quantities without reciprocal lattice units. The connection between  $k_{\min}$  and q is obvious

$$q = \frac{k_{\min}}{\pi}.$$
(4.17)

For the incommensurability  $\delta = q - 1/2$  we obtain the following expression

$$\delta = \frac{\arccos\left(\frac{-\beta}{4\gamma}\right)}{\pi} - \frac{1}{2}.$$
(4.18)

### **Programming details:**

Using Fast Fourier Transformation, we transform the solution  $p_{min}(N)$  in Fourier space and determine the Fourier coefficients

$$\Phi_n = \sum_{j=0}^{N-1} \Phi_j \cdot e^{i\frac{2\pi n}{N}j} \,. \tag{4.19}$$

The four1-routine of the numerical recipes, which is used for this purpose, requires a one-dimensional data vector data(2*N*) containing the real parts of the *N* displacements  $p_{min}(N)$  as even components and its imaginary parts as odd components. The latter are zero because the solutions for the displacements are real valued.

The modulation wave vector of the solution is given by the wave vector  $k = 2\pi n_{\text{max}}/N$  which corresponds to  $n = n_{\text{max}}$ , the *n*-value of the largest Fourier coefficient  $\Phi_n$ .

With (4.17) and (4.18) we can determine the values for the modulation wave vector q and the incommensurability  $\delta$ :

$$\delta = \frac{1}{\pi}k - \frac{1}{2} = \frac{2n_{\max}}{N} - \frac{1}{2}$$
(4.20)

## 4.1.4 Parameter analysis

In the following we analyze which values of the parameters  $\gamma$  and  $\beta$  might allow us to reproduce the experimental data for the incommensurability in Reference [80]. The calculations are based on the free energy in Fourier space in second order expansion.

### **4.1.4.1** Calculation of the onset parameter $\gamma_c = \gamma(T_{c2})$

The  $\gamma$ -term in the free energy (4.3) describes the tendency toward a spin-Peierls distortion. As mentioned in Section 3.5 the magneto-elastic coupling  $\gamma$  increases with decreasing temperature. We make the following ansatz for the temperature dependence of  $\gamma$ :

$$\gamma = \gamma_c + \alpha (T_{c2} - T) \tag{4.21}$$

We now calculate which value of  $\gamma$  corresponds to the onset temperature  $T_{c2}$ , where the phase transition from the disordered phase to the incommensurably modulated phase takes place.

In order to calculate the free energy of a modulation with the modulation wave vector  $k_{\min} = \arccos(-\beta/4\gamma)$ , we insert  $k_{\min}$  into the dispersion (4.6) of the free energy  $\Delta F = \frac{1}{2} \sum_k \omega_k |\Phi_k|^2$  in Fourier space in second order expansion

$$\begin{split} \omega_{k_{\min}} &= 1 + \gamma \cos\left(2k_{\min}\right) + \beta \cos\left(k_{\min}\right) \\ &= 1 + \gamma \cos\left(2 \arccos\left(\frac{-\beta}{4\gamma}\right)\right) - \frac{\beta^2}{4\gamma} \\ &\stackrel{4.9a}{=} 1 + \gamma \left[2\cos^2\left(\arccos\left(\frac{-\beta}{4\gamma}\right)\right) - 1\right] - \frac{\beta^2}{4\gamma} \\ &= 1 + \gamma \left[\frac{2\beta^2}{16\gamma^2} - 1\right] - \frac{\beta^2}{4\gamma} \\ &= 1 - \gamma - \frac{\beta^2}{8\gamma} \,. \end{split}$$
(4.22)

At  $T = T_{c2}$  the system does not gain energy from any displacement ( $\Delta F = 0$  for  $\forall \Phi_k$ ). Therefore,  $\omega_{k_{\min}}(\gamma(T_{c2}))$  has to be zero and we get the following expression for the onset parameter  $\gamma(T_{c2}) = \gamma_c$ 

$$\gamma_c = \frac{1}{2} \pm \frac{1}{2} \sqrt{1 - \frac{\beta^2}{2}} \,. \tag{4.23}$$

# 4.1 Simplified one-dimensional model for the description of the incommensurate phase and the lock-in transition

In order to find out which sign is physically reasonable, we investigate what happens with the dispersion  $\omega_{k_{\min}}(\gamma)$ , if we insert a  $\gamma$ -value slightly above the onset  $\gamma = \gamma_c + \epsilon$ . Since we expect to gain energy by entering the incommensurate phase, an expansion in  $\epsilon$  should lead to a negative value of the first derivative of the dispersion  $\omega_{k_{\min}}(\gamma_c)$ .

$$\begin{aligned} \frac{\partial \omega_{k_{\min}}}{\partial \gamma_c} \bigg|_{\gamma = \gamma_c} &= -1 + \frac{\beta^2}{8\gamma_c^2} \end{aligned}$$

$$= -1 + \frac{\beta^2}{2\left(1 \pm \sqrt{1 - \frac{\beta^2}{2}}\right)^2} \\ &= -1 + \frac{\beta^2}{2} \frac{\left(1 \mp \sqrt{1 - \frac{\beta^2}{2}}\right)^2}{\left(1 - \left(1 - \frac{\beta^2}{2}\right)\right)^2} \\ &= -1 + \frac{2}{\beta^2} \left(2 - \frac{\beta^2}{2} \mp 2\sqrt{1 - \frac{\beta^2}{2}}\right) \\ &= -2 + \frac{4}{\beta^2} \mp \frac{4}{\beta^2} \sqrt{1 - \frac{\beta^2}{2}} \\ &= \begin{cases} \leq 0 \text{ for } \forall \beta \in [0, \sqrt{2}] \\ \geq 0 \text{ for } \forall \beta \in [0, \sqrt{2}] \end{cases} \text{ for the upper sign} \\ \geq 0 \text{ for } \forall \beta \in [0, \sqrt{2}] \end{cases} \text{ for the lower sign} \end{aligned}$$

As we see, only the upper sign leads to a negative first derivative of  $\omega_{k_{\min}}(\gamma_c)$ .<sup>8</sup> Therefore, the relevant sign in (4.23) is "+", leading to

$$\gamma_{c,\text{analyt.}} = \frac{1}{2} + \frac{1}{2}\sqrt{1 - \frac{\beta^2}{2}}$$
 (4.25)

The intrachain coupling can now be written as a function of  $\beta$ ,  $\alpha$  and *T*:

$$\gamma = \frac{1}{2} \left( 1 + \sqrt{1 - \frac{\beta^2}{2}} \right) + \alpha (T_{c2} - T) .$$
(4.26)

<sup>&</sup>lt;sup>8</sup>The  $\beta$  values investigated in the following are all smaller than unity and, hence, element of  $[0, \sqrt{2}]$ .

### **Programming details:**

In the following we explain how the numerical value of  $\gamma_c$  is determined. In case of  $\gamma = \gamma_c$  the free energy is  $\Delta F = 0$  for any values of the displacements  $\Phi$  and the algorithm cannot find a minimum. In order to determine  $\gamma_c$ , we start the  $\gamma$ -loop, which realizes different values for the intrachain coupling  $\gamma$ , from the starting parameter  $\gamma = \gamma_c - \epsilon$ , i.e., we approach the incommensurate phase from the disordered phase below  $\gamma_c$ . The parameter  $\epsilon$  has a small positive value. We introduce a boolean variable declared with the value "TRUE". If the error message "To many iterations" occurs for a certain loop parameter  $\gamma$ , the value of the boolean variable is set to "FALSE". As soon as the boolean variable is set to "FALSE", the execution of the loop is terminated and the value of the current loop parameter is assigned to the parameter  $\gamma_c$ .

### **4.1.4.2** Calculation of the lock-in parameter $\gamma_l = \gamma(T_{c1})$

In order to determine which value of the intrachain coupling  $\gamma$  corresponds to the lock-in temperature  $T_{c1}$  for a fixed value of the interchain coupling  $\beta$ , we calculate the free energy in dependence of the intrachain coupling  $\gamma$ .

We insert the dispersions

$$\omega_{k_{\min},com} = 1 - \gamma \tag{4.27a}$$

$$\omega_{k_{\min},incom} = 1 - \gamma - \frac{\beta^2}{8\gamma} \tag{4.27b}$$

as well as the modulation amplitudes  $a_{\text{com}}$  (4.11a) and  $a_{\text{incom}}$  (4.11b) into the corresponding free energies (4.10a, 4.10b) and obtain the following free energies in the commensurate and incommensurate phase

$$\Delta F_{\min, \operatorname{com}}(\gamma) = -\frac{N}{4}(1-\gamma)^2 \tag{4.28a}$$

$$\Delta F_{\min, \text{ incom}}(\gamma) = -\frac{N}{4} \cdot \frac{2}{3} \left( 1 - \gamma - \frac{\beta^2}{8\gamma} \right)^2 \,. \tag{4.28b}$$

At the lock-in  $(\gamma(T_{c1}) = \gamma_l)$ , the free energies in the commensurate and the incommensurate phase should be equal

$$\Delta F_{\min, \operatorname{com}}|_{\gamma=\gamma_l} = \Delta F_{\min, \operatorname{incom}}|_{\gamma=\gamma_l} .$$
(4.29)

Maple13 determines the following approximate expression for the intrachain coupling  $\gamma_l$  at the lock-in

$$\gamma_l \approx \frac{1}{2} \pm \frac{1}{2} \sqrt{1 + \left(1 \pm \sqrt{\frac{3}{2}}\right) \beta^2} . \tag{4.30}$$

## 4.1 Simplified one-dimensional model for the description of the incommensurate phase and the lock-in transition

Since the intrachain coupling increases with decreasing temperature, we know that  $\gamma_l > \gamma_c$ . Therefore, we choose a "+" for the first sign. Because data shows an increasing of  $\gamma$  with increasing values of  $\beta$  (see Fig. 4.13 in Subsection 4.2.2) the second sign has to be positive as well, leading to

$$\gamma_{l,\text{approx.}} = \frac{1}{2} + \frac{1}{2} \sqrt{1 + \left(1 + \sqrt{\frac{3}{2}}\right) \beta^2} .$$
 (4.31)

### **Programming details:**

In the following we explain how the numerical value of  $\gamma_l$  is determined.

There are two possibilities to identify the value of  $\gamma$  which corresponds to the lock-in value  $\gamma_l$ . One of them is based on the examination of the modulation wave vector, the other one on the examination of the formation energy of a soliton. At this point, we will discuss the first case. The latter will be discussed in Subsection 4.2.4. However, both ways lead to the same results.

With increasing  $\gamma$  the system approaches the lock-in. At the lock-in transition to the commensurate phase the wave vector of the solution for the modulation of the displacements is q = 1/2, which corresponds to  $n_{\text{max}} = N/4$ . Therefore, we determine  $\gamma_l$  as the arithmetic average of the largest  $\gamma$ -value for which we obtain  $n_{\text{max}} \neq N/4$  and the smallest value for which we obtain  $n_{\text{max}} = N/4$ .

# 4.1.4.3 Determination of the parameters $\beta$ and $\alpha$ describing the experimental data

We already mentioned our aim to reproduce the experimental data for the incommensurability  $\delta$  published in Reference [80] (see Fig. 4.5):

$$\delta_{\exp} = -0.222(8) + 0.00040(1) \left[ K^{-1} \right] T.$$
(4.32)

Inserting the expression (4.26) for the intrachain coupling into the incommensurability (4.18), yields the following expression for the incommensurability  $\delta$  in dependence of the parameters  $\beta$  and  $\alpha$  and of the temperature *T* 

$$\delta = \frac{1}{\pi} \arccos\left(\frac{-\beta}{2\left[1 + \sqrt{1 - \frac{\beta^2}{2}} + 2\alpha(T_{c2} - T)\right]}\right) - \frac{1}{2}.$$
(4.33)

In the following, we explain how the onset value  $\delta(T_{c2}) = \delta_{\exp}(T_{c2})$  can be determined by a proper choice for the value of the interchain coupling  $\beta$  and how the parameter  $\alpha$ can be calculated by using the gradient of the fit function (4.32) to the experimental data points.



Fig. 4.5: Experimental data from Schönleber *et al.* [80] for the incommensurability  $\delta$  along the chains. The line represents a phenomenological fit to the data points:  $\delta_{exp} = -0.222(8) + 0.00040(1) \left[ K^{-1} \right] T.$ 

### Discussion of the parameter $\beta$

Schönleber *et al.* [80] reported an onset temperature  $T_{c2} = 90$  K. Inserting the onset temperature into the incommensurability (4.33), as well as the experimental onset value

$$\delta_{\exp}(T_{c2}) = -0.0222 + 0.0004 \cdot 90 = 0.0138 , \qquad (4.34)$$

leads to the following condition for the parameter  $\beta$ 

$$0.0138 = \frac{1}{\pi} \arccos\left(\frac{-\beta}{2\left(1 + \sqrt{1 - \frac{\beta^2}{2}}\right)}\right) - \frac{1}{2}.$$
(4.35)

According to Maple13, this equation is solved for the following value of the interchain coupling  $\beta$ 

$$\beta \approx 0.1727127512$$
. (4.36)

### Discussion of the parameter $\alpha$

In order to derive a condition for the parameter  $\alpha$ , we calculate the gradient of the fit function (4.32) to the experimental data points

$$\frac{\partial \delta_{\exp}}{\partial T} = 0.0004 \,. \tag{4.37}$$

For the sake of clarity, we substitute

$$x = 1 + \sqrt{1 - \frac{\beta^2}{2}} \,. \tag{4.38}$$

Using  $\frac{d}{dy} \arccos(y) = -\frac{1}{\sqrt{1-y^2}}$  for |y| < 1, the gradient of (4.33) can be written as

$$\frac{\partial \delta}{\partial T} = \frac{\partial}{\partial T} \left\{ \frac{1}{\pi} \arccos\left(\frac{-\beta}{2\left[x + 2\alpha(T_{c2} - T)\right]}\right) - \frac{1}{2} \right\}$$

$$= \frac{1}{\pi} \frac{-1}{\sqrt{1 - \frac{\beta^2}{4}\left(x + 2\alpha(T_{c2} - T)\right)^{-2}}} \cdot \left(\frac{-\beta}{2}\right) \cdot \frac{(-2\alpha) \cdot (-1)}{\left(x + 2\alpha(T_{c2} - T)\right)^2}$$

$$= \frac{\beta \alpha}{\pi} \cdot \frac{1}{\sqrt{\left(x + 2\alpha(T_{c2} - T)\right)^4 - \frac{\beta^2}{4}\left(x + 2\alpha(T_{c2} - T)\right)^2}}.$$
(4.39)

The interchain coupling range  $\gamma_c \leq \gamma \leq \gamma_l$  within which the incommensurate phase occurs is really small (see Section 4.2.2). Within the interval  $[\gamma_c, \gamma_l]$ , the incommensurability  $\delta$  (4.33) depends virtually linear on the interchain coupling  $\gamma$  or on the temperature *T*, respectively (see examples in Fig. 4.6).

Therefore, we assume that the gradient  $\partial \delta / \partial T \approx \text{const}$  and independent of *T*, which allows us to approximate the gradient of the incommensurability  $\delta$  with the gradient at  $T = T_{c2}$ .

Equating the gradient (4.37) of the fit function to the experimental data points with (4.39) at  $T = T_{c2}$  leads to the following approximate expression for the parameter  $\alpha$  in dependence of the interchain coupling  $\beta$ 

$$\alpha \approx 0.0004 \cdot \frac{\pi}{\beta} \cdot \sqrt{x^4 - \frac{\beta^2}{4}x^2} \,. \tag{4.40}$$

We obtain the following formula to convert the intrachain coupling  $\gamma$  to the temperature

$$T = \frac{\gamma_c - \gamma}{\alpha} + T_{c2} \,. \tag{4.41}$$

However, we have to keep in mind that this formula requires a virtually linear intrachain coupling dependence of the incommensurability  $\delta$ . For a non-linear intrachain coupling dependence, formula (4.41) is not valid anymore.



Fig. 4.6: Interchain coupling dependence of the analytically determined incommensurability  $\delta = \frac{1}{\pi} \arccos\left(\frac{-\beta}{4\gamma}\right) - \frac{1}{2}$  for the smallest and the largest value of the, in the following investigated, interchain couplings  $\beta$  within the intrachain coupling interval  $[\gamma_c, \gamma_l]$ .

## 4.2 Results and discussion

### 4.2.1 Spatial dependence of the displacements

### 4.2.1.1 Display of the solutions

In the simplified model of a single spin chain, the even sites correspond to one of the original spin chains, while the odd sites correspond to the other chain. We always display the solutions for the original spin chains.

In order to explain how the solutions are displayed, we have a look at the selection of an arbitrary solution for the commensurate and incommensurate modulation of the displacements, as shown in Figures 4.7a and 4.7b.



Fig. 4.7: Spatial dependence of the displacements. (a) Commensurate modulation with displacements of the same amplitude but alternating signs on neighboring sites. (b) Incommensurate modulation with two domain walls. The black points designate the sites where neighboring Ti ions displace in the same direction.

In the commensurate phase neighboring Ti sites are shifted by the same amplitude, but alternating sign. In the incommensurate phase domain walls are created. At the position of a domain wall, the alternation of the sign of the displacements changes its pattern so that neighboring sites displace with a very small amplitude in the same direction (see black points in Fig. 4.7b). We see that a domain wall corresponds to a zero of the envelope of the modulation, as it is the case for the solitons in the adaptive solution for the incommensurate modulation in Figure 2.8 in Section 2.4.2.

In general, the solutions imply a large number of solitons. Thus, for clarity we plot the solutions multiplied by the factor  $(-1)^i$ . This modification has the advantage that dis-

placements of neighboring sites have the same sign and changes in the displacement amplitudes become obvious. Finding the position of the solitons is quite easy since we just have to look for changes in the sign of the amplitudes. Figure 4.8 shows the modification of the solutions displayed in Figure 4.7.



Fig. 4.8: Modified spatial dependence of the displacements. (a) Commensurate modulation with displacements of the same amplitude but alternating signs on neighboring sites. (b) Incommensurate modulation with two domain walls. The black points designate the sites where solitons are located.

#### 4.2.1.2 Solutions in the commensurate and incommensurate phase

In Figures 4.11 and 4.12 the spatial dependence of the displacements is shown for a selection of  $\gamma$ -values for the interchain couplings  $\beta = 0.1727127512$  and  $\beta = 0.4327127512$ . With increasing interchain coupling the number of solitons increases in the solutions. In the following discussion, we concentrate on the solution for  $\beta = 0.1727127512$ . The shape of the solutions curves for this coupling is clearer than for higher interchain couplings due to the comparatively small number of solitons.

For the sake of completeness, the solutions for  $\beta = 0.4327127512$  are displayed as well because later on we discuss all quantities for this value of the interchain coupling.

The full width half maximum of the solutions is larger than for the initial vectors. The modulation amplitude of the solutions is slightly smaller than the initial vector amplitude. The reason for this discrepancy is that the solutions are not strictly sinusoidal. The fourth order term in the free energy, which disfavors large amplitudes, was only included in the calculation of the initial vector amplitude but not in the calculation of the initial vector amplitude but not in the calculation of the initial vector amplitude but not in the solution of the initial vector itself (see Section 4.1.2). The true minimum of the free energy is reached for a solution with a slightly smaller modulation amplitude.

With increasing intrachain coupling  $\gamma$  the solutions become less sinusoidal but more boxshaped and the amplitude of the box plateau equates the modulation amplitude in the commensurate phase. These observations are in accordance with the properties of incommensurably modulated phases in canonical spin-Peierls compounds (see Subsection 2.4.2), where close to the lock-in transition to the commensurate phase a pure sinusoidal modulation does not give an appropriate description of the displacements anymore [40].

However, the spatial dependence of the displacements has some characteristics which have not been reported in the canonical scenario: At the sites where the displacement amplitude of the initial vectors is maximal, the solutions form little "ears", where the amplitude is much higher than in the commensurate case. The origin of this ears can be explained with regard to the staggered nature of the spin chains in the titanium oxyhalogenides.



Fig. 4.9: Displacements in the commensurate phase.

We will now discuss the origin of an ear in the red chain. In the commensurate case, neighboring Ti ions within the chains displace with maximal amplitude in opposite directions (see Fig. 4.9). Due to the magneto-elastic coupling between the chains, the green Ti ions pull the interjacent red Ti ion in the other chain in opposite directions.



Fig. 4.10: Displacements in the incommensurate phase.

In the incommensurate phase, however, solitons are present in the solutions. If we compare the solutions for the different chains, we note that ears in the red chain occur at the sites where the displacement amplitude in the green chain becomes zero, i.e., where

a soliton is located in the green chain. As already explained in the previous subsection, these sites correspond to the situation that two neighboring green Ti ions displace in the same direction (see Fig. 4.10). Therefore, the interjacent red Ti ion in the other chain experiences a force in only one direction, resulting in a displacement with an amplitude higher than in the commensurate case.



Fig. 4.11: Spatial dependence of the displacements  $\Phi[i]$  for intrachain couplings far away from the lock-in in the incommensurate phase. Only the first 600 Ti sites are displayed. Green and red lines correspond to the different Ti chains. The initial vectors are only displayed for the red curve.





Fig. 4.11: Spatial dependence of the displacements  $\Phi[i]$  for intrachain couplings close to the lock-in in the incommensurate phase. Only the first 600 Ti sites are displayed. Green and red lines correspond to the different Ti chains. The initial vectors are only displayed for the red curve.



Fig. 4.11: Spatial dependence of the displacements  $\Phi[i]$  for an intrachain coupling (e) just before the lock-in in the incommensurate phase and (f) at the lock-in in the commensurate phase. Only the first 600 Ti sites are displayed. Green and red lines correspond to the different Ti chains. The initial vectors are only displayed for the red curve.





Fig. 4.12: Spatial dependence of the displacements  $\Phi[i]$  for intrachain couplings far away from the lock-in in the incommensurate phase. Only the first 600 Ti sites are displayed. Green and red lines correspond to the different Ti chains. The initial vectors are only displayed for the red curve.



Fig. 4.12: Spatial dependence of the displacements  $\Phi[i]$  for intrachain couplings close to the lock-in in the incommensurate phase. Only the first 600 Ti sites are displayed. Green and red lines correspond to the different Ti chains. The initial vectors are only displayed for the red curve.



Fig. 4.12: Spatial dependence of the displacements  $\Phi[i]$  for an intrachain coupling (e) just before the lock-in in the incommensurate phase and (f) at the lock-in in the commensurate phase. Only the first 600 Ti sites are displayed. Green and red lines correspond to the different Ti chains. The initial vectors are only displayed for the red curve.





Fig. 4.13:  $\gamma_c$ - and  $\gamma_l$ -values determined by numerics and analytical curves for the onset parameter  $\gamma_c$  and the lock-in parameter  $\gamma_l$ . The numerical data points are determined for 0.1727127512  $\leq \beta \leq 0.4327127512$  with a step size  $\Delta \beta = 0.02$  while the analytical curves are displayed for  $\beta \in [0, 0.5]$ .

For small interchain couplings, for example for  $\beta = 0.1727127512^{9}$ , the parameter range  $\gamma_c \leq \gamma \leq \gamma_l$  within which the incommensurate phase occurs is quite small (see Fig. 4.13). Therefore, it might be more convenient to analyze the incommensurate phase for a larger value of  $\beta$ , as long as we do not want to reproduce experimental data.

In Figure 4.13 we can see that the numerically determined values for the onset parameter  $\gamma_c$  lie well on the analytical curve  $\gamma_{c,\text{analyt.}}(\beta)$  (4.25), while the values for the lock-in parameter  $\gamma_l$  lie all above the approximate curve  $\gamma_{l,\text{approx.}}(\beta)$  (4.31).

This is not surprising. As mentioned in the previous subsection, the calculations in the incommensurate phase are not exact because the solutions are not strictly sinusoidal. The numerically determined modulation amplitudes in the incommensurate phase are

<sup>&</sup>lt;sup>9</sup>This is the  $\beta$ -value which has to be chosen in order to reproduce the experimentally determined onset value for the incommensurability  $\delta$  (see Subsection 4.1.4.3)

slightly smaller than the analytically calculated amplitudes (4.11b) and the true minimum  $\Delta F_{\text{incom}}|_{\gamma=\gamma_l}$  of the free energy in the incommensurate phase is slightly lower than  $\Delta F_{\min, \text{incom}}|_{\gamma=\gamma_l \text{ amprox}}$ .

Therefore, even for intrachain coupling values  $\gamma$  slightly larger than  $\gamma_{l,approx}$  the free energy of the incommensurate solution is lower than the energy minimum of the commensurate solution. The stabilization of the incommensurate phase leads to  $\gamma_l > \gamma_{l,approx}$ .

Furthermore, we see in Figure 4.14 that there is no difference in the  $\gamma_c$ - and  $\gamma_l$ -values for different values of the parameter  $a_0$ . This justifies the usage of the rescaled couplings  $\gamma$  and  $\beta$  instead of  $a_1$  and b which we have anticipated and discussed already in Section 4.1.



Fig. 4.14:  $\gamma_c$ - and  $\gamma_l$ -values determined by numerics for various values for the parameter  $a_0$ . The data points lie perfectly on top of each other.

# 4.2.3 Intrachaincoupling and temperature dependence of the incommensurability $\delta$



Fig. 4.15: Experimental results for the temperature dependence of the incommensurabilities along ( $\delta$ ) and perpendicular ( $q_1$ ) to the chains. (Figure taken from Ref. [80])

In Figure 4.16 we see the numerically determined temperature dependence of the incommensurability for various values of the interchain coupling  $\beta$ .

For the conversion of the intrachain coupling  $\gamma$  to the temperature *T* we used formula (4.41) (see Subsection 4.1.4.3).

As expected, the incommensurability increases with increasing temperature. At the transition temperature  $T_{c1}$  the incommensurability suddenly drops to zero. However, it is not clear, if the decrease is truly discontinuous or if it just seems to be discontinuous, due to the finite step size with which the intrachain coupling  $\gamma$  is increased (for example  $\Delta\gamma(\beta = 0.43) \approx 0.00037$ ). We also have to keep in mind that we investigate a system of finite size  $N < \infty$ .

Within the incommensurate phase, the incommensurability does not show the linear temperature dependence observed in experiment (see Fig. 4.15). Actually, the numerically determined data rather resembles to the experimental data for the incommensurability  $q_1$  perpendicular to the chains.

If we compare the results for  $\beta = 0.1727127512$  with the experimental results, we see that this value of  $\beta$  leads to a far too small temperature range for the incommensurate phase. The numerically determined lock-in temperature  $T_{c1} = 89, 15$  K is by far larger than the experimental determined temperature  $T_{c1,exp.} = 67$  K.



Fig. 4.16: Numerical results for the temperature dependence of the incommensurability  $\delta$  for various values of the interchain coupling  $\beta$ .

In view of the lack of a linear relationship between  $\delta$  and  $\gamma$ , it does not surprise that we cannot reproduce the correct lock-in temperature. The determination of the formula to convert the intrachain coupling  $\gamma$  to the temperature *T* (4.41) in Subsection 4.1.4.3 required a linear intrachain coupling dependence of the incommensurability. Because this relationship is not valid in the numerically determined data, the usage of formula (4.41) is not reasonable anymore.

In summary, we can say that the one-dimensional model does not allow us to reproduce experimental data. The similarity of the numerically determined data for the incommensurability  $\delta$  to the experimental data for the incommensurability  $q_1$  perpendicular to the chains suggests that two-dimensional effects might play a more important role than expected and that the one-dimensional model is too simple to describe the experiment.

Since we are not able to reproduce experimental data and since the range of the incommensurate phase is much broader for larger values of  $\beta$  (see Fig. 4.17a as well as Subsection 4.2.2), from here on, we analyze all quantities for the interchain coupling  $\beta = 0.4327127512$ .



Fig. 4.17: (a) Numerical results for the dependence of the incommensurability  $\delta$  on the intrachain coupling  $\gamma$  for various values of the interchain coupling  $\beta$ . (b) Numerical results for the dependence of the incommensurability  $\delta$  on the intrachain coupling  $\gamma$  for  $\beta = 0.4327127512$ 

## 4.2.4 Study of the 1-kink-solution

4.2.4.1 Formation energy of a soliton: 1-kink-energy  $\Delta E_{1kink}$ 



Fig. 4.18: Formation energy of a soliton in dependence of the intrachain coupling  $\gamma$ . Green points indicate the values of  $\gamma$  for which the spatial dependence of the displacements are displayed in Figure 4.20.

In the incommensurate phase, a finite number of solitons is created. The system gains energy by creating a soliton as long as this energy gain is not overcome by the repulsive interaction energy between the created solitons. A discussion of the formation energy of a single soliton gives information about the point at which the system has to pay for creating a soliton and, therefore, enters the commensurate phase.

Accordingly, the 1-kink-energy  $\Delta E_{1kink}$  changes its sign at the lock-in transition to the commensurate phase. A study of the spatial dependence of the displacements in the vicinity of a soliton allows us to analyze on which length scale the solitons interact.

As we can see in Figure 4.18, as well as in Figure 4.20, for intrachain couplings  $\gamma \leq$  1.01297 the algorithm for the minimization is able to find the true minimum instead of getting lost in local minima. Although an initial vector has been chosen, which realizes

just four kinks<sup>10</sup> in the spatial dependence of the displacements, the solutions have far more kinks (see Fig. 4.20a and 4.20b). As already mentioned in Subsection 4.1.2, for some reason, the minimization algorithm is sometimes able to increase the number of domain walls predefined by the initial vectors.

For  $\gamma \ge 1.01334$  the algorithm gets lost in the local minimum of the 1-kink-solution.

Coming closer to the lock-in at  $\gamma_l = 1.12513$ , it should be less and less favorable for the system to become incommensurate, i.e., to create solitons.

Therefore, we expect a monotonic growth of the 1-kink-energy in dependence of the intrachain coupling  $\gamma$ . However, this behavior is only observed for intrachain couplings  $\gamma \ge 1.0537871$ .

For  $1.01334 \le \gamma \le 1.0537871$  the 1-kink-energy decreases with increasing  $\gamma$ . Since we are mainly interested in the behavior of  $\Delta E_{1kink}$  for intrachain couplings close to the lock-in value, we will not discuss this decreasing part of the 1-kink-energy curve.

Close to the lock-in, the 1-kink-energy increases virtually linear with the intrachain coupling  $\gamma$  (see Fig. 4.19).



Fig. 4.19: Formation energy of a soliton in dependence of the intrachain coupling  $\gamma$  close to the lock-in value  $\gamma_l = 1.12513$ .

<sup>&</sup>lt;sup>10</sup>Due to periodic boundary conditions, the smallest number of kinks which can be realized in the solutions is four (see "Programming details").



Fig. 4.20: Spatial dependence of the displacements  $\Phi[i]$  for an initial vector which corresponds to the solution with the smallest number of kinks. Green and red lines correspond to the different Ti chains. The N/2 = 1024 sites per chain are displayed. The initial vectors are only displayed for the red curve.
#### **Programming details:**

The energy gained from or payed for the creation of a soliton is calculated as the difference between the local energy minimum for the 1-kink-solution  $E_{513} = \Delta F(n = 513)$  and the local energy minimum of the commensurate solution  $E_{512} = \Delta F(n = 512)$ .  $E_{513}$  and  $E_{512}$  are the energy minima determined by using the initial vector for n = N/4 + 1 = 513and n = N/4 = 512. Note that we use *n* instead of  $n_{min}$  or  $n_{max}$  here, i.e., we do NOT refer to true minima and no Fast Fourier Transformation is performed.

Because of periodic boundary conditions the solitons are created in pairs (see Fig. 2.6 in Section 2.4). Accordingly, the smallest number of solitons per chain is two. Since the numerically determined solution for the modulation of the displacements implies information about both chains<sup>*a*</sup>, the smallest number of solitons which can be realized is four (see Fig. 4.20).

Accordingly, in order to calculate the formation energy of a single soliton, the above mentioned energy difference has to be divided by a factor of four

$$\Delta E_{1\rm kink} = \frac{E_{513} - E_{512}}{4} \,. \tag{4.42}$$

With the study of the 1-kink-energy we obtain a second possibility to determine the lockin value  $\gamma_l$  of the intrachain coupling. At the lock-in, the 1-kink-energy changes its sign because the creation of a soliton is not favorable anymore.

Therefore, we determine  $\gamma_l$  as the arithmetic average of the largest  $\gamma$  value for which  $E_{1kink} < 0$  and the smallest value for which  $E_{1kink} \ge 0$ .

Both ways to determine the lock-in parameter  $\gamma_l$ , i.e., the determination of  $\gamma_l$  via the 1-kink-energy on the one hand, and via the modulation wave vector on the other hand (see Subsection 4.2.2), lead to the same results (see Fig. 4.21).

<sup>*a*</sup>The spatial dependence of the displacements is always plotted separately for the two chains as described in Subsection 4.2.1.1.



Fig. 4.21: Values of  $\gamma_l$ , determined by the study of the modulation wave vector q or by the examination of the 1-kink-energy, respectively, and approximate values for the lock-in parameter  $\gamma_l$ .

#### **4.2.4.2 Soliton energy** $\Delta W$

The total energy  $\Delta W$  of a finite number of solitons is given by the formation energy gained from or payed for the creation of the solitons and the interaction energy between the solitons. The interaction energy of the solitons depends on the inter-soliton spacing or the soliton density, respectively, and therewith on the number of solitons within a system of given size.

Since the solitons are created in quartets, the number p of solitons is determined by

$$p = 4 \cdot \Delta n = 4 \cdot \left( n_{\max} - \frac{N}{4} \right) . \tag{4.43}$$

The soliton-soliton distance *d* within a single chain of the length N/2 is given by

$$d = \frac{N}{2p} \,. \tag{4.44}$$

With an increasing number of solitons the inter-soliton spacing decreases while the interaction energy between the solitons increases.

In the incommensurate phase, we gain energy from the creation of each single soliton, while we have to pay energy for the creation of each single soliton in the commensurate phase. Therefore, the formation energy of the solitons depends linearly on the soliton number p = N/2d.

According to Nakano and Fukuyama [52], the spatial dependence of the displacement  $\Phi(x)$  for soliton excitations is given by a hyperbolic tangent (see Section 2.4.2.1). Therefore, we assume an exponential decrease of the soliton-soliton interaction energy with increasing inter-soliton spacing. The length scale on which the solitons can interact is determined by the soliton width  $\xi_d$ .

We fit the numerically determined data for the soliton energy  $\Delta W$  in dependence of the soliton-soliton distance *d* by the following function

$$f(d) = \frac{N}{2d} \left( \Delta E_{1\text{kink}} + u_d \cdot e^{-\frac{d}{\xi_d}} \right) .$$
(4.45)

The values of the fit parameters  $u_d$  and  $\xi_d$  are calculated with GnuPlot.

### **Programming details:**

For each value of the intrachain coupling  $\gamma$ , we determine the soliton energy  $\Delta W$  as the difference between the true energy minimum  $\Delta F(n_{\text{max}})$  of a solution with  $p = 4\Delta n$  solitons and the local energy minimum for the commensurate solution  $E_{512}$ , i.e., the solution in absence of solitons:

$$\Delta W = \Delta F(n_{\max}) - E_{512} \tag{4.46}$$

 $\Delta W$  is plotted versus the soliton-soliton distance  $d = N/8\Delta n$ .



Fig. 4.22: Soliton energy  $\Delta W$  in dependence of the soliton-soliton distance d for the intrachain coupling  $\gamma = 1.08$  far away from the lock-in. The parameters  $u_d$  and  $\xi_d$  are calculated with GnuPlot. The percentage errors are given in brackets.



Soliton energy for N=2048 β=0.43, γ=1.12456

Fig. 4.22: Soliton energy  $\Delta W$  in dependence of the soliton-soliton distance d for the intrachain coupling  $\gamma = 1.12456$  close to the lock-in in the incommensurate phase. The parameters  $u_d$  and  $\xi_d$  are calculated with GnuPlot. The percentage errors are given in brackets. Figure (c) shows a fit of the numerically data within the d range bounded by the red square in Figure (b).





Fig. 4.22: Soliton energy  $\Delta W$  in dependence of the soliton-soliton distance *d* for the intrachain coupling  $\gamma = 1.12494$  just before the lock-in in the incommensurate phase. The parameters  $u_d$  and  $\xi_d$  are calculated with GnuPlot. The percentage errors are given in brackets. Figure (e) shows a fit of the numerically data within the *d* range bounded by the red square in Figure (d).



Fig. 4.22: Soliton energy  $\Delta W$  in dependence of the soliton-soliton distance d for the intrachain coupling  $\gamma = 1.12531$  at the lock-in in the commensurate phase. The parameters  $u_d$ and  $\xi_d$  are calculated with GnuPlot. The percentage errors are given in brackets. Figure (g) shows a fit of the numerically data within the d range bounded by the red square in Figure (f).

In Figure 4.22 the soliton energy  $\Delta W$  is displayed in dependence of the soliton-soliton distance *d* for various values of the intrachain coupling  $\gamma$ .

The soliton energy diverges for vanishing inter-soliton spacing since the repulsive interaction energy between the solitons becomes exponentially large.

In the incommensurate phase (see Figs. 4.22a-e), the energy minimum of  $\Delta W$  is reached for a finite value of the soliton-soliton distance *d*.

In the commensurate phase (see Figs. 4.22f-g), however, the energy minimum  $\Delta W = 0$  is reached in the limit of infinite soliton-soliton distance  $d \to \infty$ , i.e., for a vanishing number of solitons.

The fit function  $f(\delta)$  (4.45) fits very well to the numerically determined  $\Delta W(d)$  dependence. That corroborates the assumption that an exponentially increasing mutual repulsion of the solitons exists.

In the following subsection the values determined for the soliton width  $\xi_d$  are compared with the soliton width  $\xi_{\Phi}$ , extracted from the examination of the spatial dependence of the 1-kink-solution.

#### 4.2.4.3 Spatial extent of a soliton

In order to learn more about the length scale on which the solitons interact, we will study the 1-kink-solution with regard to the spatial extent of a soliton.

As already mentioned, the spatial dependence of the displacements close to the lock-in is given by a hyperbolic tangent (2.13) [52] (see Section 2.4.2.1).

Therefore, we fit the 1-kink-solution in the vicinity of a soliton by the following function

$$\Phi(x) = \pm \Phi_0 \tanh\left(\frac{x}{2\xi_{\Phi}}\right). \tag{4.47}$$

We can rewrite (4.47) in terms of the exponential function  $e^{-x/\xi}$ :

$$\begin{split} \Phi(x) &= \pm \Phi_0 \frac{e^{\frac{x}{2\xi\Phi}} - e^{-\frac{x}{2\xi\Phi}}}{e^{\frac{x}{2\xi\Phi}} + e^{-\frac{x}{2\xi\Phi}}} \\ &= \pm \Phi_0 \frac{1 - e^{-\frac{x}{\xi\Phi}}}{1 + e^{-\frac{x}{\xi\Phi}}} \,. \end{split}$$

For large values of *x*, i.e., not too close to the position of the soliton, the exponential function is very small and the expansion  $(1 + \epsilon)^{-1} \approx 1 - \epsilon + \mathcal{O}[\epsilon^2]$  leads to the following expression

$$\Phi(x) \approx \pm \Phi_0 \left( 1 - 2e^{-\frac{x}{\xi_{\Phi}}} + \mathcal{O}\left[ \left( e^{-\frac{x}{\xi_{\Phi}}} \right)^2 \right] \right) \,. \tag{4.48}$$

We see now that the introduction of the factor 2 in the denominator of the argument of the hyperbolic tangent in (4.47) allows for a direct comparison of the soliton width  $\xi_{\Phi}$  with the value of the soliton width  $\xi_d$ , determined in the previous section from the exponential decrease of the soliton-soliton interaction. Without this factor, we would get an exponential function  $e^{-2x/\xi'_{\Phi}}$  with doubled argument and we would determine the soliton width  $\xi'_{\Phi} = 2\xi_d$ .

The question arises if we can find a proper fit for the spatial dependence of the displacements in the second chain, too. Therefore, we investigate the effect of the displacements in the first chain on the displacements in the second chain.

In the commensurate phase, the displacements in the two different chains are independent because the interchain coupling term in the free energy vanishes. In the 1-kinksolution, the displacements are locally still independent, however, in the vicinity of a soliton in one of the chains, the displacements in the other chain are affected, too.

The displacements in the different chains seem to be independent from each other as long as the the differences in the amplitudes of the displacements are all zero, i.e., as long as the gradients are zero.

Approaching a soliton, the gradient of the displacements in the first chain increases, reaches its maximum where the soliton is actually located and decreases again with increasing distance to the soliton. The same behavior can be observed for the absolute values of the displacements in the second chain.

Therefore, we assume that the spatial dependence of the displacements in the second chain can be described by the derivative of the spatial dependence of the displacements in the first chain. Adding an offset and including a proportionality constant, the 1-kink-solution for the second chain can be fitted by the following function

$$\Phi_2(x) = -\Phi_{\text{off}} - \frac{c \cdot \Phi_0}{2\xi_{\Phi} \cosh^2\left(\frac{x}{2\xi_{\Phi}}\right)} \,. \tag{4.49}$$

For the parameters  $\Phi_0$  and  $\xi_{\Phi}$ , the values determined for the first chain are inserted.

We can see in Figure 4.23 that the hyperbolic tangent fits very well to the plot for the spatial dependence of the soliton. Also the line shape of the plot for the spatial dependence of the displacements in the second chain is very well captured by the corresponding fit function.

### **Programming details:**

Since the parameter *x* in (4.47) corresponds to the distance to the position of a soliton, we display the displacements  $\Phi$  in dependence of  $\Delta i = i - i_{\text{Soliton}}$ , the distance to the site  $i_{\text{Soliton}}$ , where a soliton is located.

The position of a soliton corresponds to a zero in the displacements. Since the displacements are either positive or negative, we choose  $i_{\text{Soliton}}$  as the arithmetic average of the two sites where the displacement changes its sign.

In the present case we study the spatial dependence of the displacements in the vicinity of a soliton which is located at  $i_{Soliton} = 127.5$ .

For the second chain we have to keep in mind that the sites are shifted by half a lattice constant against the first chain. The maximal displacement amplitude in the second chain, corresponding to the soliton in the first chain, is therefore located at  $i_{2,Soliton} = 127$ .



β =0.43 γ=1.08, n=513





Fig. 4.23: Spatial dependence of a soliton for various intrachain couplings  $\gamma$ . Blue and pink lines correspond to the different Ti chains. The parameters  $\Phi_0$ ,  $\Phi_{\text{off}}$ , *c* and the soliton width  $\xi_{\Phi}$  are calculated with GnuPlot. The percentage errors are given in brackets.



β =0.43 γ=1.12494, n=513



Fig. 4.23: Spatial dependence of a soliton for various intrachain couplings  $\gamma$ . Blue and pink lines correspond to the different Ti chains. The parameters  $\Phi_0$ ,  $\Phi_{\text{off}}$ , c and the soliton width  $\xi_{\Phi}$  are calculated with GnuPlot. The percentage errors are given in brackets.

Intrachain coupling $\gamma$	ξd	$\xi_{d, ext{zoom}}$	$\xi_{\Phi}$	$\xi_d/\xi_{\Phi}$	$\xi_{d,\text{zoom}}/\xi_{\Phi}$
1.08000	2.1424	-	1.5550	1.38	-
1.10022	1.9984	1.9255	1.4466	1.38	1.33
1.10322	1.9722	1.8950	1.4342	1.38	1.32
1.10621	1.9530	1.8522	1.4187	1.38	1.31
1.10921	1.9343	1.8206	1.4054	1.38	1.30
1.11221	1.9161	1.7742	1.3925	1.38	1.27
1.11520	1.8983	1.7250	1.3800	1.38	1.25
1.11820	1.8809	1.6725	1.3678	1.38	1.22
1.11970	1.8724	1.6450	1.3619	1.37	1.21
1.12119	1.8639	1.5945	1.3560	1.37	1.18
1.12269	1.8556	1.5383	1.3502	1.37	1.14
1.12307	1.8535	1.5367	1.3488	1.37	1.14
1.12344	1.8515	1.5077	1.3474	1.37	1.12
1.12381	1.8494	1.5061	1.3460	1.37	1.12
1.12419	1.8402	1.4751	1.3445	1.37	1.10
1.12456	1.8382	1.4736	1.3431	1.37	1.10
1.12494	1.8433	1.4399	1.3417	1.37	1.07
1.12531	1.8413	1.5749	1.3403	1.37	1.18
Arithmetic average	1.9003	1.6445	1.3822	1.37	1.20

Tab. 4.1: Comparison of the values of the soliton width  $\xi_d$  and  $\xi_{d,zoom}$  in the fits for the soliton energy  $\Delta W$  and the values of the soliton width  $\xi_{\Phi}$  in the fits for the spatial dependence of the 1-kink-solution for various values of the intrachain coupling  $\gamma$  (The shaded region highlights the  $\gamma$  value in the commensurate phase).

In Table 4.1 the values of the soliton width  $\xi_{\Phi}$ , determined by the investigation of the spatial dependence of the 1-kink-solution, are compared with the values for  $\xi_d$  and  $\xi_{d,zoom}$ , extracted from the investigation of the soliton energy  $\Delta W$  (see Subsection 4.2.4.2). Table 4.1 also comprises values of the intrachain coupling  $\gamma$  for which the corresponding fits are not displayed in Figures 4.23 and 4.22.

If we compare the arithmetic averages of the values for the soliton width ratios  $\xi_d/\xi_{\Phi} = 1.37$  and  $\xi_{d,\text{zoom}}/\xi_{\Phi} = 1.20$ , we see that the latter soliton widths are in quite good agreement. That makes sense because  $\xi_{d,\text{zoom}}$  was extracted from the fits of the soliton energy  $\Delta W$  in a soliton-soliton distance range of  $\Delta d = 100$  (see Fig. 4.22c, e and g), which corresponds to the  $\Delta i$  range  $-50 \le \Delta i \le 50$  in the 1-kink-solution within which a soliton is actually located (see Fig. 4.23).

Approaching the lock-in from the incommensurate phase ( $\gamma \leq 1.12494$ ), the agreement between the soliton widths  $\xi_{d,zoom}$  and  $\xi_{\Phi}$  becomes better and better. That could be caused by the decreasing soliton density with approaching the lock-in. The spatial dependence of the displacements minimizing the free energy  $\Delta F$  becomes more and more box-shaped (see Fig. 4.12). Therefore, also the 1-kink-solutions resemble more and more the box-shaped initial vectors (see Fig. 4.20).

The jump between the last two values of the ratio  $\xi_{d,\text{zoom}}/\xi_{\Phi}$  in Table 4.1 arises because the system enters the commensurate phase, where no solitons are created.

### 4.2.4.4 Soliton energy and the incommensurability $\delta$

The soliton energy  $\Delta W$  can be plotted versus the incommensurability  $\delta$  as well. Using formula (4.20), we can rewrite the incommensurability  $\delta$  in terms of  $\Delta n$ :

$$\delta = q - \frac{1}{2}$$

$$= \frac{2n_{\max}}{N} - \frac{2\frac{N}{4}}{N}$$

$$= \frac{2\Delta n}{N}.$$
(4.50)

Therewith, we obtain the following relationships to the soliton number p and the soliton-soliton distance d, respectively

$$p = 2\delta N \tag{4.51}$$

$$d = \frac{1}{4\delta} \,. \tag{4.52}$$

By analogy with (4.45) we fit the numerically determined data by the fit function

$$f(\delta) = 2\delta N \left( \Delta E_{1\text{kink}} + u_{\delta} \cdot e^{-\frac{1}{4\xi_{\delta}\delta}} \right) .$$
(4.53)



Fig. 4.24: Soliton energy  $\Delta W$  in dependence of the incommensurability  $\delta$  for the intrachain coupling  $\gamma = 1.08$  far away from the lock-in. The parameters  $u_{\delta}$  and  $\xi_{\delta}$  are calculated with GnuPlot. The percentage errors are given in brackets.



Fig. 4.24: Soliton energy  $\Delta W$  in dependence of the incommensurability  $\delta$  for the intrachain coupling  $\gamma = 1.12456$  close to the lock-in in the incommensurate phase. The parameters  $u_{\delta}$  and  $\xi_{\delta}$  are calculated with GnuPlot. The percentage errors are given in brackets. Figure (c) shows a fit of the numerically data within the  $\delta$  range bounded by the red square in Figure (b).



Fig. 4.24: Soliton energy  $\Delta W$  in dependence of the incommensurability  $\delta$  for the intrachain coupling  $\gamma = 1.12494$  just before the lock-in in the incommensurate phase. The parameters  $u_{\delta}$  and  $\xi_{\delta}$  are calculated with GnuPlot. The percentage errors are given in brackets. Figure (e) shows a fit of the numerically data within the  $\delta$  range bounded by the red square in Figure (d).



Fig. 4.24: Soliton energy  $\Delta W$  in dependence of the incommensurability  $\delta$  for the intrachain coupling  $\gamma = 1.12531$  at the lock-in in the commensurate phase. The parameters  $u_{\delta}$ and  $\xi_{\delta}$  are calculated with GnuPlot. The percentage errors are given in brackets. Figure (g) shows a fit of the numerically data within the  $\delta$  range bounded by the red square in Figure (f).

In Figure 4.24 the soliton energy  $\Delta W$  is plotted versus the incommensurability  $\delta$  for various values of the intrachain coupling  $\gamma$ .

In the incommensurate phase (see Figs. 4.24a-e), the minimum of  $\Delta W$  is reached for a finite value of the incommensurability  $\delta = \delta_{\text{opt},\Delta W}$ .

For incommensurabilities  $\delta < \delta_{\text{opt},\Delta W}$ , the soliton energy is mainly determined by the linear term proportional to the 1-kink-energy  $\Delta E_{1\text{kink}}$ . The system gains energy from creating more and more solitons while the repulsive soliton-soliton interaction energy is almost negligible.

However, for  $\delta > \delta_{\text{opt},\Delta W}$  the exponentially increasing soliton-soliton interaction energy is of more significance and the total soliton energy  $\Delta W$  starts to increase.

At the  $\delta$ -value where  $\Delta W$  changes its sign, the soliton-soliton interaction energy overcomes the soliton formation energy.

In the commensurate phase (see Figs. 4.24f-g) the system has to pay energy for the creation of each single soliton. The soliton energy minimum is therefore  $\Delta W = 0$  for  $\delta_{\text{opt},\Delta W} = 0$ . With increasing incommensurability  $\delta$  the soliton energy diverges due to the hardcore repulsion of the solitons.

The incommensurability  $\delta_{\text{opt}}$  which corresponds to the energy minimum of  $\Delta W$  is the one realized in the solutions of the minimization of the free energy (see Section 4.2.3). Therefore we determine  $\delta_{\text{opt},\Delta W}$  and compare its intrachain coupling dependence with the results for the incommensurability  $\delta$  discussed in Section 4.2.3.

In Figure 4.25 we see that the data points for  $\delta(\gamma)$  and  $\delta_{\text{opt},\Delta W}(\gamma)$  lie perfectly on top of each other, as expected.



Fig. 4.25: Numerical results for the dependence of the incommensurability  $\delta$  and the incommensurability  $\delta_{\text{opt},\Delta W}$  on the intrachain coupling  $\gamma$  for  $\beta = 0.4327127512$ .

In the following we will investigate the order of the phase transition at  $\gamma_l$  from the incommensurate to the commensurate phase.

In Figure 4.25 the incommensurability drops discontinuously to zero at  $\gamma_l = 1.12513$ . The intrachain coupling  $\gamma$  is increased with a finite step size, and it is hard to decide, whether the decrease of the incommensurability at  $\gamma_l$  is really discontinuous or if the step size is just to large to display a continuous decrease. Also the finite system size  $N < \infty$  may play a role.

Close to the lock-in, the relationship between the intrachain coupling  $\gamma$  and the 1-kinkenergy  $\Delta E_{1kink}$  is virtually linear (see Fig. 4.19 in Section 4.2.4.1). Therefore, we can study the dependence of the incommensurability  $\delta_{opt}$  on  $\Delta E_{1kink}$ , in order to gain more information about the discontinuous drop of the incommensurability at the lock-in transition.

We determine a formula for  $\delta_{opt}$ , based on the minimization of the fit function (4.53) with respect to  $\delta$ .

First of all, we will approximate an analytical solution for  $\delta_{opt}$  in dependence of the 1-kink-energy  $\Delta E_{1kink}$ .

Introducing the parameter  $\lambda = 1/(4\xi_{\delta}\delta)$  with the derivative  $\partial\lambda/\partial\delta = -\lambda/\delta$  leads to

$$\frac{\partial f(\delta)}{\partial \delta} = 2N \cdot \Delta E_{1\text{kink}} + 2N \cdot u_{\delta}(1+\lambda)e^{-\lambda} .$$
(4.54)

In order to determine the incommensurability  $\delta_{\text{opt}}$  for which the soliton energy  $f(\delta)$  becomes minimal, we determine the zeros of (4.54)

$$0 = \Delta E_{1\text{kink}} + u_{\delta}(1 + \lambda_{\text{opt}})e^{-\lambda_{\text{opt}}}$$

Assuming that the second summand is mainly determined by the exponential function, we approximate the factor  $(1 + \lambda_{opt}) \approx (1 + \lambda_0)$  with a constant value for  $\lambda_0$ . We obtain the following expression for  $\delta_{opt}$  in dependence of the 1-kink-energy  $\Delta E_{1kink}$ 

$$\delta_{\text{opt}} = \frac{1}{4\xi_{\delta} \ln\left(\frac{u_{\delta}(1+\lambda_0)}{-\Delta E_{1\text{kink}}}\right)} \,. \tag{4.55}$$

In the incommensurate phase the 1-kink-energy  $\Delta E_{1kink}$  is negative and the argument of the logarithm is positive. Coming closer to the lock-in, the 1-kink-energy  $\Delta E_{1kink}$  approaches zero and the argument of the logarithm diverges.

Therefore, close to the lock-in, the incommensurability  $\delta_{opt}$  decreases continuously, but really fast, with increasing 1-kink-energy  $\Delta E_{1kink}$ .

In order to find out how well the numerically determined data points ( $\Delta E_{1\text{kink}}, \delta_{\text{opt},\Delta W}$ ) are described by the approximated solution for  $\delta_{\text{opt}}$ , we fit  $\delta_{\text{opt}}$  to these data points.

We have to keep in mind, that the parameters  $\xi_{\delta}$  and  $u_{\delta}$  and, hence, the parameter  $\lambda_0$  are different for various values of the 1-kink-energy  $\Delta E_{1kink}$ . However, close to  $\Delta E_{1kink} = 0$  these dependencies can be neglected.

Furthermore, the choice of the parameters  $u_{\delta}$  and  $\lambda_0$  in (4.55) is not unambiguous. Therefore, we combine these parameters to the new fit parameter  $a = u(1 + \lambda_0)$ .<sup>11</sup>

In Figure 4.26 we see that the continuous  $\delta_{\text{opt}}$ -curve fits very well to the data points. The value of the fit parameter for the soliton width,  $\xi = 1.6022$ , is in good agreement with the average soliton width  $\overline{\xi}_{d,\text{zoom}} = 1.6445^{-12}$  in Table 4.1. The consistency of  $\delta_{\text{opt}}$  with the data points suggests that the discontinuous drop of  $\delta_{\text{opt},\Delta W}$  is a finite step size effect.

Hence, we are certain that the nature of the lock-in transition in our model is continuous and governed by a logarithm.



Fig. 4.26: Fit of the approximated solution for  $\delta_{\text{opt}}$  to the numerical results for the  $\Delta E_{1\text{kink}}$  dependence of the incommensurability  $\delta_{\text{opt},\Delta W}$ .

<sup>&</sup>lt;sup>11</sup>In order to distinguish between the fit parameters  $\xi_{\delta}$  and  $u_{\delta}$  in Figure 4.24 and the fit parameters in Figure 4.26, we refer to the latter as  $\xi$  and u

<sup>&</sup>lt;sup>12</sup> $\overline{\xi}_{d,\text{zoom}}$  should be pretty much identical to the soliton width  $\overline{\xi}_{\delta,\text{zoom}}$  because the corresponding fit functions f(d) and  $f(\delta)$  can be converted into each other.

In order to check the plausibility of the approximation  $(1 + \lambda_{opt})e^{-\lambda_{opt}} \approx (1 + \lambda_0)e^{-\lambda_{opt}}$ used for the determination of  $\delta_{opt}$  (4.55), we minimize  $f(\delta)$  numerically <sup>13</sup> for various values of the 1-kink-energy  $\Delta E_{1kink}$ .

For the parameters  $\xi_{\delta}$  and  $u_{\delta}$  we insert the values for  $\xi$  and u of the preceding fit. The parameter u was not directly determined in the preceding fit, but can be extracted from the fit parameter  $a = u(1 + \lambda_0)$ .

In order to calculate *u*, we resubstitute  $\lambda = 1/(4\xi\delta)$ 

$$u = \frac{a}{1 + \frac{1}{4\xi\delta}} \,. \tag{4.56}$$

We estimate the value of  $\delta$  with the average incommensurability  $\overline{\delta} = 0.02$  within the investigated 1-kink-energy range  $-0.002 \le \Delta E_{1kink} \le 0$  and receive

$$u = 0.1871224347$$
.



Fig. 4.27: Approximated solution for  $\delta_{\text{opt}}$  and numerically determined values for  $\delta_{\text{opt},f(\delta)}$  in dependence of the 1-kink-energy  $\Delta E_{1\text{kink}}$ . The  $(\Delta E_{1\text{kink}}, \delta_{\text{opt},f(\delta)})$  data points are displayed with a line, in order to highlight the difference between the two curves.

<sup>&</sup>lt;sup>13</sup>The minimization was implemented in Maple13.

In Figure 4.27 we see that coming closer to the lock-in, there is only a very small difference between the  $\delta_{\text{opt}}$ -curve and the  $\delta_{\text{opt},f(\delta)}$ -data points, resulting from the numerical minimization. Both curves show the continuous decrease of the incommensurability at  $\Delta E_{1\text{kink}} = 0$ . Therefore, we can assume that the approximated solution for  $\delta_{\text{opt}}$  gives a good description of the characteristics of the incommensurability close to the lock-in.

For the sake of completeness, the numerical results for  $\delta_{\text{opt},\Delta W}$  and  $(\Delta E_{1\text{kink}}, \delta_{\text{opt},f(\delta)})$  are displayed in Figure 4.28. Again we see a very satisfactory agreement between the data sets.



N=2048, β=0.43

Fig. 4.28: Numerically determined values for  $\delta_{\text{opt},\Delta W}$  and  $\delta_{\text{opt},f(\delta)}$  in dependence of the 1-kink-energy  $\Delta E_{1\text{kink}}$ .

All in all, we conclude that the drop of the incommensurability at the lock-in at  $\gamma_l$  and, hence, the phase transition to the commensurate phase is continuous in contrast to the first order phase transition observed in experiments, which corresponds to a discontinuous decrease of the incommensurability  $\delta$ .

However, these results are consistent with the results for the soliton-distance *d* dependence of the soliton energy  $\Delta W$  in Section 4.2.4.2. A first order phase transition occurs in presence of a soliton attraction (see Section 2.4.2). Such an attraction would lead to a

decrease of the soliton energy  $\Delta W$  at very large values of the soliton-soliton distance *d*, which cannot be observed in our data (see Fig. 4.22).

Furthermore, the non-sinusoidal character of the spatial dependence of the displacements close to the lock-in transition implies the continuous character of the lock-in phase transition in the scope of the numerically determined data.

In Section 2.4.2, it was shown that the first order phase transition observed in experiments is only captured in theory, if the modulation is pure sinusoidal. The examination of the adaptive solution for the modulations leads to a continuous phase transition.

Moreover, the non-sinusoidal character of the solutions implies the admixture of Fouriercomponents so that, strictly speaking, the displacements are not anymore described by a single Fourier-component.

In Section 2.4.2 was also reported, that the admixture of Fourier-components might lead to a continuous phase transition in the scope of a Ginzburg-Landau expansion of the free energy, in accordance with the above discussed results.

### **5** Conclusion and Outlook

In the present thesis, we followed the phenomenological approach to describe the incommensurate phase in the titanium oxyhalogenides within a Ginzburg-Landau theory, proposed by Rückamp *et al* [9].

Rückamp *et al* discussed the free energy in second order expansion. They noted that fourth order terms have to be included since the second order expansion would favor infinite amplitudes of the displacements of the Ti ions.

The aim of the present thesis was therefore to discuss the free energy in fourth order expansion. As expected, this extension allowed us to capture the lock-in transition from the incommensurate to the commensurate phase.

We discussed a one-dimensional model of two frustrated spin chains.

In Section 4.2.1, the spatial dependence of the displacements within the incommensurate and the commensurate phase has been studied.

The presence of solitons in the incommensurably modulated solutions could be corroborated as well as the finding that the solutions closer to the lock-in transition are not pure sinusoidal anymore [40]. This implies the condition to the appearance of a continuous phase transition in the numerically determined data in contrast to the first order phase transition observed in experiments.

Furthermore, the appearance of little "ears" in the solutions, at the sites where a soliton is located in the other spin chain, was discussed. These have not been reported to appear in the spatial dependence of the displacements in canonical spin-Peierls compounds and were attributed to the fact that the Ti chains in the titanium oxyhalogenides are shifted against each other by half a lattice constant. This leads to the situation that at the sites, where a soliton is located in one chain, neighboring Ti ions pull the interjacent Ti ion in the other chain in the same direction, resulting in a larger amplitude of the displacement at these sites than in the commensurate phase, where neighboring Ti ions displace in opposite directions.

In Section 4.2.2, we analyzed the range  $\gamma_c \leq \gamma \leq \gamma_l$  of the intrachain coupling  $\gamma$ , which is related to the temperature within which the incommensurate phase occurs. At the onset parameter  $\gamma_c$  the system enters the incommensurate phase, while the lock-in parameter  $\gamma_l$  indicates the phase transition to the commensurate phase.

We found a broadening of the  $[\gamma_c, \gamma_l]$  interval with increasing interchain coupling  $\beta$ . For the  $\beta$ -value which has to be chosen in order to reproduce experimental data, the  $[\gamma_c, \gamma_l]$  interval was found to be too small to describe the experiment.

Moreover, the results for the determined  $\gamma$ -values were independent of the parameter  $a_0$ , the prefactor of the local term  $\sum_i \Phi_i \Phi_i$  in the free energy  $\Delta F$ . We rescaled the free energy

#### 5 Conclusion and Outlook

and showed that the two remaining independent parameters were the rescaled couplings  $\gamma$  and  $\beta$ .

The intrachain coupling  $\gamma$  and temperature dependence of the incommensurability  $\delta$  was investigated in Section 4.2.3. The numerically determined data displayed the main characteristics of the experimental data for the incommensurability along the chains, such as the decrease of the incommensurability with decreasing temperature and the lock-in transition to the commensurate phase, where the incommensurability vanishes.

However, the numerical data did not show the linear temperature dependence observed in experiments and the lock-in temperature determined from the numerical data was by far too large. This was attributed to the fact, that the formula to convert the intrachain coupling to the temperature was based on the linear intrachain coupling dependence of the incommensurability. Since this dependence was not obtained for the numerical data, the conversion was not reasonable anymore.

In fact the numerically determined data for the incommensurability  $\delta$  resembled more the experimental data for the incommensurability  $q_1$  perpendicular to the chains, which was not discussed within our model. This suggested that the one-dimensional model is too simple to describe the experiment.

Our aim to reproduce experimental data in a quantitative scope obviously failed.

In the following, we therefore chose a value of the interchain coupling  $\beta$  which corresponded to a broader interval of the incommensurate phase and we concentrated on a detailed description of the physics close to the lock-in transition.

In Section 4.2.4, we discussed the formation energy  $\Delta E_{1kink}$  of a soliton, which is negative in the incommensurate phase, where the system gains energy from the creation of a soliton, and which is positive in the commensurate phase, where the system has to pay for creating a soliton.

We calculated the lock-in value of the intrachain coupling  $\gamma_l(\beta)$  by determining the zeros of the 1-kink-energy. The obtained values were found to be consistent with the results for the lock-in couplings, determined by investigating the modulation wave vector of the spatial dependence of the displacements, which was performed in Section 4.2.2.

Close to the lock-in, the dependence of the 1-kink-energy on the intrachain coupling was found to be virtually linear.

Subsequently, we determined the soliton energy  $\Delta W$ , which consists of the formation energy of the solitons and of the soliton-soliton interaction energy.

While the former depends linearly on the number of created solitons, the latter decreases exponentially with the inter-soliton spacing.

A formula for the dependence of the soliton energy on the soliton-soliton distance *d* was set up and fitted to numerical data. Thereby, we were able to determine the soliton width  $\xi_d$ , which determines the length scale on which the solitons interact.

In order to compare this length scale with the spatial extent of a soliton, we studied the spatial dependence of the 1-kink-solution in the vicinity of a soliton.

In canonical spin-Peierls compounds the spatial dependence of the displacements is given

by a hyperbolic tangent [52] (see Section 2.4.2.1). Therefore, we fitted the numerically determined displacements in the vicinity of a soliton sitting in one of the chains to a hyperbolic tangent. The spatial dependence of the displacements in the other chain were fitted to the derivative of the hyperbolic tangent.

The determined values for the soliton width  $\xi_{\Phi}$  were in good agreement with the determined values for  $\xi_d$ . The agreement became better closer to the lock-in.

Furthermore, we investigated the soliton energy in dependence of the incommensurability  $\delta$ . We determined the optimal incommensurability  $\delta_{opt}$  by minimizing the soliton energy with respect to  $\delta$ . The obtained values were in perfect accordance with the results for the incommensurability  $\delta$  obtained by the investigation of the modulation wave vector of the spatial dependence of the displacements, performed in Section 4.2.3.

A comparison of the numerically determined data with an approximate formula for the 1-kink-energy dependence of the incommensurability  $\delta_{opt}$  allowed us to identify the discontinuous drop of the incommensurability  $\delta$  at the lock-in as a finite step size effect.

We found the phase transition from the incommensurate phase to the commensurate phase to be continuous, which is in accordance with the finding that adaptive solutions for the spatial dependence of the displacements in canonical spin-Peierls compounds lead to a continuous phase transition to the commensurate phase [46].

The question arises, what is actually responsible for the first order character of the phase transition from the incommensurate to the commensurate phase observed in experiments [8]. An explanation could be the existence of a weak attractive interaction between the solitons, which might not be described in our one-dimensional model. Such a soliton attraction was proposed to be responsible for first order incommensurate-commensurate phase transitions in canonical spin-Peierls compounds [49, 50].

All in all, we conclude that our model is not able to reproduce experimental data quantitatively. However, our results show that the incommensurate phase in the titanium oxyhalogenides, which is induced by a frustrated interchain coupling, shows the same characteristics as the incommensurate phase induced by applying a magnetic field on canonical spin-Peierls compounds.

It is very interesting that the numerically determined behavior of the incommensurability  $\delta$  along the chains rather resembles the experimental data for the incommensurability  $q_1$  perpendicular to the chains. Since the numerically determined  $\delta(\gamma)$  dependence is obviously not given by an arc cosine it might be interesting to modulate the displacements with a logarithmic modulation instead of the sinusoidal modulation.

Extending our model to two dimensions, i.e. investigating a large number of frustrated spin chains, as it was originally proposed by Rückamp *et al*, may allow to reproduce experimental data in a quantitative way.

Finally, we want to mention that Abel *et al.* [64] recently developed a model, which leads to a picture for the observed sequence of phase transitions which is in perfect accordance with our results.

## Appendix

# A.1 Computational details

Number of $\beta$ -loop runs:	13
Number of $\gamma$ -loop runs per $eta$ -loop run:	484
Average run time per $\gamma$ -loop:	4 s
Average run time per $\beta$ -loop:	50 min
Total run time:	7 h
Average number of iterations for arbitrary <i>n</i> :	45
Average number of iterations for $n = n_{min}$ :	18

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## Erklärung

Hiermit erkläre ich, dass die vorliegende Arbeit von mir selbstständig angefertigt wurde, außer den angegebenen Quellen keine weiteren Hilfsmittel benutzt wurden und Zitate kenntlich gemacht wurden.

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