Theoretical study of the magnetism in the incommensurate phase of TiOCl

D.M. Mastrogiuseppe *, M.E. Torio, C.J. Gazza, A.O. Dobry

Facultad de Ciencias Exactas Ingeniería y Agrimensura,
Universidad Nacional de Rosario and Instituto de Física Rosario,
Bv. 27 de Febrero 210 bis., 2000 Rosario, Argentina

Abstract

Going beyond a recently proposed microscopic model [1] for the incommensurate transition in the spin-Peierls TiOX (X=Cl, Br) compounds, in the present work we start by studying the thermodynamics of the model with XY spins and adiabatic phonons. We find that the system enters in an incommensurate phase by a first order transition at a low temperature \( T_{c1} \). At a higher temperature \( T_{c2} \) a continuous transition to a uniform phase is found. Furthermore, we study the magnetism in the incommensurate phase by Density Matrix Renormalization Group (DMRG) calculations on a 1D Heisenberg model where the exchange is modulated by the incommensurate atomic position pattern. When the wave vector \( q \) of the modulation is near \( \pi \), we find local magnetized zones (LMZ) in which spins abandon their singlets as a result of the domain walls induced by the modulated distortion. When \( q \) moves far away enough from \( \pi \), the LMZ disappear and the system develops incommensurate magnetic correlations induced by the structure. We discuss the relevance of this result regarding previous and future experiments in TiOCl.

Key words: Spin-Peierls; TiOCl; DMRG

PACS: 75.10.Pq; 75.40.Mg; 64.70.Rh

1. Introduction

The interest on spin-Peierls systems [2] has been renewed with the recent discovery of a dimerization in the TiOX (X = Cl, Br) compounds family. In them, the magnetically active Ti ions connected by O ones are arranged in a bilayer structure. Ti ion positions on a layer are shifted with respect to the other neighboring layer, forming something like an anisotropic triangular structure. Initially postulated for a resonating valence bond state [3], TiOCl turned out to be mainly a one-dimensional magnetic system [4] with the Ti \( d_{xy} \) orbitals pointing towards each other in the crystallographic \( b \) direction [5]. The high temperature magnetic susceptibility is well described by the Bonner-Fisher curve, indicating a nearest neighbor magnetic exchange \( J \sim 660 K \) [5]. The peculiar ingredient in the TiOCl phase diagram is the appearance of an incommensurate intermediate phase between the high temperature uniform phase and the low \( T \) dimerized phase [5,6] commonly found in a regular spin-Peierls system. The transition temperatures were experimentally found to be \( T_{c1} \sim 66 K \) and \( T_{c2} \sim 92 K \). In Ref. [6] a very large energy gap of about 430K in the low temperature phase and a pseudo spin gap below 135K have been also reported.

The origin of the intermediate phase remains controversial and not well understood yet. The shifted positions of a Ti ion in a chain between the two neighboring chains, make it plausible to entail that some type of competition between the in-chain and out-of-chain interactions could be the origin of the incommensurate...
Some of us recently proposed a microscopic mechanism for the incommensurate phase [1], where the antiferromagnetic Ti chains are immersed in the phonon bath of the bilayer structure. By using the Cross-Fisher theory [7], it was shown that the geometrically frustrated character of the lattice is responsible for the structural instability, leading the chains to an incommensurate phase without an applied magnetic field. For TiOCl, our results showed consistency with the temperature dependence of the phonon frequencies and the value of the incommensuration vector at the transition temperature. Moreover, we found that the dynamical structure factor shows a progressive softening of an incommensurate phonon near the zone boundary as the temperature decreases, along with a broadening of the peak. These features are in agreement with the experimental inelastic X-ray measurements [8].

The purpose of this work is double. As a first step we present the phase diagram as a function of the temperature of the model proposed in Ref. [1]. On the other hand, we theoretically analyze the evolution of the magnetism inside the incommensurate phase by solving a one-dimensional Heisenberg model with a first order character of the first transition [8,9] experimentally found in TiOCl can therefore be accounted for spinel ferromagnets by means of the Jordan-Wigner transformation. The resulting pseudofermion-phonon model is solved in a finite system by diagonalizing the one-electron problem in the background of a deformed lattice.

Now we consider deformations of the form:

\[ u_{i,j} = u_0 \cos(q \cdot R_{i,j} - \pi/4), \] (3)

where the wave vector \( q = (0, q) \) is constrained to the chain direction and \( R_{i,j} \) is the position vector in the two-dimensional Bravais lattice. We have chosen the \( \pi/4 \) phase to have a continuous energy at \( q = \pi \). The total free energy per site is:

\[ f = \frac{u_0^2 M \omega^2(q)}{2} - \frac{T}{N_s} \sum_{\gamma=1}^{N_s} \ln(1 + e^{-\lambda \gamma/T}), \] (4)

where \( T \) is the temperature in units of \( J \) and \( \omega^2(q) = \frac{1}{2\pi^2} [K_{\text{in}} \sin^2(q R_{i,j}) + K_{\text{inter}} (1 - \cos(q R_{i,j}) \cos(q R_{j,i}))] \) is the dispersion relation of the two-dimensional phonons.

We have minimized \( f \) with respect to \( u_0 \) and \( q \) at different temperatures. The results are shown in Fig. 1. At low temperatures a dimerized phase is found. This is the usual result for an isolated spin-Peierls chain. At the first transition temperature \( T_{c1} \), \( u_0 \) jumps discontinuously and \( q \) moves away from \( \pi \). This is a structural incommensurate phase which arises as a competition between the tendency to the dimerization of each chain and the frustration in the elastic interchain coupling. The value of \( q \) remains constant up to a second temperature \( T_{c2} \) where \( u_0 \) vanishes and the system becomes uniform. The sequence of the two transitions and the first order character of the first transition [8,9] experimentally found in TiOCl can therefore be accounted by our model. However the precise fitting of the parameters is a quite complex task which would need the inclusion of the z-component of the spin interaction and the non adiabatic effects of the phonons [10].
3. Magnetic structure in the incommensurate phase

The feature that makes the compound under study different from an usual spin-Peierls system is the appearance of an incommensurate phase without an applied magnetic field. It is therefore quite important to characterize the magnetism in this phase. As no magnetic interchain interaction was included in the model (1), we will consider a one-dimensional Heisenberg model as given by (2) with deformation fixed by (3). The model will be solved by DMRG. We will focus on the local magnetization and spin-spin correlation functions.

As a reference state to discuss the results, we take the dimerized phase because the structural deformation (3) with q near π can be thought as a smooth modulation of the dimer pattern. In a dimerized phase the spins are paired in singlets and the local magnetization is zero. There is a gap in the spectrum and the magnetic correlation declines exponentially. When the pattern (3) is included with \( q = \pi (1 - \frac{2l}{N_s}) \) to have an integer number of wavelengths in the chain, the dimerization phase changes its sign 2l times as we travel along the chain from one extreme to the other (see the gray line of Fig. 2). When l is small enough, the situation has some similarities with the domain walls (or solitons) appearing in the presence of a high magnetic field in regular spin-Peierls systems [11]. We expect that for each zero of (3) free LMZ should appear. This is in fact the situation we found in Fig. 2a, b and c where the mean value \( \langle S_i^z \rangle \) is shown. We see the appearance of LMZ in all the zeros of the deformation except in the first, which is greatly affected by the proximity to the edge. These LMZ are seen as clouds of polarized spins emerging from the singlet background. Moreover, they are uncorrelated among them because their distances are longer than the correlation length of the dimerized phase. These LMZ are paired in singlets and the local magnetization is zero. There is a gap in the spectrum and the magnetic correlation declines exponentially. When the pattern that minimize the free energy.

state. They are randomly orientated. We expect that the magnetic susceptibility will be affected by these LMZ. It should increase compared to the dimerized phase. This feature has been experimentally observed in TiOCl [8].

When \( q_1 \) moves further away from \( \pi \), the zeros of (3) fall within a distance of the order of the correlation length and the LMZ disappear as seen in Fig. 2d. For comparison we show the result of a uniform Heisenberg model (UHM) a quite different behavior than that expected. Note that \( C(|i-j|) \) for \( q_4 \) approaches the one of the UHM, a quite different behavior than that of \( q_1, q_2 \) and \( q_3 \). We will undertake a careful analysis of the magnetic correlation function in a forthcoming paper.

A more dramatic change in the behavior of \( C(|i-j|) \) is found for \( q_4 \) where the LMZ do not appear. In this case the correlation decreases more slowly than in the previous cases. For comparison we show the result of a uniform Heisenberg model (UHM) where the quasi-long range antiferromagnetic order is expected. Note that \( C(|i-j|) \) for \( q_4 \) approaches the one of the UHM, a quite different behavior than that of \( q_1, q_2 \) and \( q_3 \). We will undertake a careful analysis of this long distance behavior for different modulations in a forthcoming paper.

More importantly, there is a modulation of the long distance behavior with half the wavelength of that which has the imposed structure. The magnetic structure can no longer be interpreted in terms of a weak
perturbation of the dimerized state. Instead, the magnetism becomes incommensurate as a response to the modulated exchange. In some sense, the situation is the dual to the one recently studied in some multiferroic materials [12]. There, an helical magnetic structure induces a lattice distortion which finally produces the ferroelectricity, whereas in our case the lattice distortion is the driving force which produces an incommensurability of the magnetic state.

These features are even more apparent in the structure factor $S(q)$ shown in Fig. 3b. For $q_1$, $q_2$ and $q_3$ there is a single maximum at $q_{\max } = \pi$ whose intensity decreases as $q$ moves away from $\pi$. This maximum is rounded as in a pure dimerized chain [13]. It can be fitted near $q = \pi$ by the law $\frac{1}{(\pi - q)^2 + \xi^2}$ (corresponding to a free massive boson propagator [14]) with $\xi \sim 3.3$. This asserts our previous statement that imposing distortions with wavevector $q_i$ near enough to $\pi$, the long range magnetic correlation behaves as in a dimerized chain, decreasing exponentially with a correlation length of the order of $\xi$. For $q_i = q_4$ the behavior changes qualitatively. Two additional maxima appear at one side and the other of the highest peak at $\pi$, corresponding to the long distance magnetic modulation found in $C(|i - j|)$ at $T_c$ [14]. Moreover, the peak at the center is not longer rounded but it behaves similarly to the UHM. This signals a tendency towards a quasi-long range incommensurate magnetic correlation of the system. Let us make a brief discussion about the application of these results to TiOCl. As measured from X-ray experiments [8,9], the modulation wave vector is $q \sim 3.05$ at $T_c$ and it moves slightly to $\pi$ when decreasing the temperature towards $T_s$, where it jumps discontinuously to $\pi$. So we expect a change of the magnetic behavior inside the incommensurate phase from a structure with LMZ to another without LMZ but with an incommensurate correlation function. This should be checked in future magnetic experiments.

In summary we have found that a system with one-dimensional antiferromagnetic chains coupled to two-dimensional phonons in an anisotropic triangular lattice accounts for the appearance of the incommensurate phase in TiOCl. The magnetism in this intermediate state includes uncorrelated LMZ near the dimerized phase, and incommensurate correlations with no LMZ towards the uniform phase. In the last case, the modulation found in the correlation function is related to the modulation of the imposed distortion by a factor of two in their wavelengths.

This work was supported by ANPCyT (PICT 1647), Argentina.

References

[1] D. Mastrogiuseppe and A. Dobry, arXiv:0810.3018v1.
[2] J. W. Bray et al., Extended linear chain compounds, edited by J. S. Miller, Plenum, New York 1983, Vol 3, pp 353-415.
[3] R. Beynon and J. Wilson, J. Phys.: Condens. Matter 5, 1983 (1993).
[4] M. Shaz et al., Phys. Rev. B. 71, 10045(R) (2005).
[5] A. Seidel, C. A. Marianetti, F. C. Chou, G. Ceder, P. A. Lee, Phys. Rev. B 67, 020405(R) (2003).
[6] T. Imai and F. C. Chou, arXiv:cond-mat/0301425v1.
[7] M.C. Cross and D.S. Fisher, Phys. Rev. B 71, 214304 (2007).
[8] E. T. Abel et al., Phys. Rev. B 65, 020405(R) (2003).
[9] A. Krimmel et al., Phys. Rev. B. 73, 172413 (2006).
[10] A. O. Dobry, D. C. Cabra, and G. L. Rossini, Phys. Rev. B 75, 045122 (2007).
[11] A. E. Feiguin, J. A. Riera, A. Dobry, and H. A. Ceccatto, Phys. Rev. B 56, 14607 (1997). Note that in the case studied in this reference, states with finite magnetization were considered whereas in the present case no magnetic field is applied and the LMZ add up to give a zero total $S_z$ state.
[12] I. A. Sergienko and E. Dagotto, Phys. Rev. B 73, 094434 (2006).
[13] R. Chitra et al., Phys. Rev B 52, 6581 (1995).
[14] S. R. White and I. Affleck, Phys. Rev. B 54, 9862 (1996).