The chiral charge density wave transition in 1T-TiSe$_2$

Jasper van Wezel
Materials Science Division, Argonne National Laboratory, Argonne, IL 60439, USA
E-mail: jvanwezel@anl.gov

Abstract. It was recently suggested that the formation of charge density wave order in 1T-TiSe$_2$ is accompanied by the emergence of orbital order, which renders the combined state chiral. Here, we analyse the transition between the chiral and non-chiral phases of TiSe$_2$ in terms of a Ginzburg-Landau description. We find that the phase transition is expected to be of second order, and that the consequences of the formation of chiral charge order should be observable in a variety of experimental settings.

1. Introduction
In the layered transition metal dichalcogenide 1T-TiSe$_2$, the formation of charge order was recently suggested to give rise to a chiral pattern of electronic density [1–3]. The spiral order consists of three charge density wave components, which are shifted in phase with respect to each other. As a result, the dominant propagation vector of the charge ordered state is rotated as one goes from one atomic layer to the next. Similar chiral phases are common in magnetically ordered materials, where the order parameter is a vector whose rotation around a propagation direction straightforwardly yields a spiral magnetization [4]. In the case of charge order however, it is not a priori clear how the scalar electronic density can be molded into a helical configuration.

This apparent paradox may be resolved by the realization that the formation of chiral charge order in TiSe$_2$ is accompanied by the simultaneous emergence of orbital order. The coupling between electronic density, orbital occupation and lattice deformation yield a chiral pattern in the combined charge and orbital ordered state [3]. Here, we discuss the transition from the non-chiral into the chiral phase in terms of a Ginzburg-Landau expansion of the free energy. We also discuss various experiments in which the transition into the combined state of chiral charge and orbital order may be observed.

2. Chiral charge and orbital order in TiSe$_2$
The quasi-two dimensional, layered material titanium-diselenide is either a semimetal or a semiconductor with a small indirect (positive or negative) band gap of the order of 150 meV or less [5, 6]. The valence band is derived predominantly from Se-4$p$ orbitals, and has its maximum at the center of the first Brillouin zone, as indicated in figure 1. The conduction band has minima at the centers of the three inequivalent zone boundaries, and consist predominantly of Ti-3$d$ electrons. Although the electron pockets are poorly nested [7], TiSe$_2$ forms a commensurate 2x2x2 charge density wave at 202 K, accompanied by a periodic lattice distortion.

In spite of many theoretical and experimental investigations, it is still unclear whether the emergence of charge order in TiSe$_2$ is driven by a variant of the Jahn-Teller effect [7–10], the
Figure 1. Left: Schematic indication of the Fermi surface pockets in the first Brillouin zone of TiSe$_2$. The three propagation vectors of the charge density modulations connect the central Se hole pocket with the Ti electron pockets at the L points. Right: The orbitals involved in the charge transfer processes of each of the three charge density wave components. The layer of Ti atoms (squares) is sandwiched between two layers of Se atoms (circles and diamonds). The resulting polarization directions of the corresponding displacement waves are indicated.

formation of an excitonic insulator [11–14], or a combined mechanism involving cooperation between excitons and phonons [15–17]. Regardless of the relative importance of phonons or excitons, it is clear that the emergence of charge order in TiSe$_2$ is associated with the transfer of electronic weight from the central Se pocket to the Ti pockets at the Brillouin zone boundaries.

2.1. Orbitals and atomic displacement
The charge density wave in TiSe$_2$ consists of three component waves, with three distinct propagation vectors, which connect the central Se pocket in figure 1 to the three inequivalent Ti pockets. The electrons in each of these pockets have a specific orbital character, which can be determined for example from a tight binding fit to the band structure [3]. As indicated in figure 1, the electrons in the Ti pockets are predominantly of the $t_{2g}$ type, and their orientation rotates as one goes from one pocket to the next. Likewise, the orientations of the Se-$p$ orbitals rotates as one goes around the central hole pocket.

Because the charge order is due to the transfer of charge between a specific Ti-$d$ orbital and its neighboring Se-$p$ orbitals, the atomic displacements $\delta \mathbf{x} \propto \epsilon \cos(\mathbf{Q} \cdot \mathbf{x})$ associated with the charge density modulations along $\mathbf{Q}$ will be confined to the plane containing these orbitals, as indicated in figure 1. We thus find that the polarizations of the atomic displacement waves accompanying the three components of the charge density wave in TiSe$_2$ are all transversal.

The total displacement pattern in the charge ordered phase consists of the superposition of three differently polarized components with three distinct propagation vectors. Having found both the propagation vectors and the polarization vectors, we still need to consider the possibility of nonzero relative phase differences between the superposed components of the displacement wave: $\delta \mathbf{x} \propto \sum_i \epsilon_i \cos(\mathbf{Q}_i \cdot \mathbf{x} + \phi_i)$. These phase differences cannot be found from the electronic band structure alone. They instead depend on the interactions between charge density wave components, which are mediated both by Coulomb interactions and coupling to the lattice.

2.2. Relative phases
To describe the emergence of relative phases, we start from the expression for the Landau free energy of a charge density modulation $\alpha = \Re\{\psi_1 + \psi_2 + \psi_3\}$ consisting of three components $\psi_j(x) = \psi_0 e^{iQ_j \cdot x + i\phi_j}$, where $Q_j$ are given by the propagation vectors of the charge ordered state: $F = \int d\mathbf{x} [a(x)\alpha^2 + b(x)\alpha^3 + c(x)\alpha^4 + d(x) (|\psi_1\psi_2|^2 + |\psi_2\psi_3|^2 + |\psi_3\psi_1|^2)]$. The spatial variation of the coefficients reflects the periodicity of the lattice as well as the internal structure of the unit cell. This can be achieved by expanding the coefficients according to
\( a = a_0 + a_1 \sum_i e^{iG_i \cdot \mathbf{x}} + \alpha \gamma \sum_{i,j} e^{iG_i \cdot (\mathbf{x} + \mathbf{R}_j)} + \ldots \), where \( \mathbf{G}_i \) are reciprocal lattice vectors, and \( \mathbf{R}_j \) connect a Titanium atom to its Selenium neighbors in the same unit cell [18]. Notice that \( \gamma \) may in general be different from one because it depends on the specific values of the electron-phonon coupling on the Ti and Se sites. Inserting this form of the coefficients into the free energy, the integrals can be evaluated directly [3]. The final expression is then found to be:

\[
F = \frac{3}{2} a_0 \psi_0^2 + \frac{1}{2} a_1 \psi_0^2 (1 - \gamma) \sum_j \cos(2\varphi_j) + \frac{3}{8} (15c_0 + 8d_0) \psi_0^4 + \frac{3}{4} c_2 \psi_0^4 \sum_j \cos(2\varphi_j - 2\varphi_{j+1}). \tag{1}
\]

Minimizing this expression with respect to the phase variables yields two possible solutions. The first is the well known non-chiral triple-\( Q \) charge density wave with all phases equal to \( \pi/2 \). There is however also a second solution, which has \( \varphi_1 = \pi/2, \varphi_2 = -\varphi_3 \), and \( \varphi_3 = \pm 1/2 \cos^{-1}[(3c_2 \psi_0^2 - 2a_1 (1 - \gamma))/(6c_2 \psi_0^2)] \). This solution corresponds to the recently observed chiral state [1–3]. It has the lowest overall energy if the argument of the cosine is larger than \(-1\), as can be seen from the comparison of the Landau free energy expressions in the presence of these phase values:

\[
F_{\text{non-chiral}} = \frac{3}{2} a_0 \psi_0^2 + \frac{3}{8} (15c_0 + 8d_0) \psi_0^4 - \frac{3}{2} a_1 \psi_0^2 (1 - \gamma) + \frac{9}{4} c_2 \psi_0^4
\]

\[
F_{\text{chiral}} = \frac{3}{2} a_0 \psi_0^2 + \frac{3}{8} (15c_0 + 8d_0) \psi_0^4 - \frac{a_1^2 (1 - \gamma)^2}{6c_2} - \frac{9}{8} c_2 \psi_0^4. \tag{2}
\]

Since the chiral state requires at least a finite value of the order parameter amplitude \( \psi_0 \), a phase diagram is implied where the uniform, high temperature state first goes into the usual non-chiral triple-\( Q \) structure at a critical temperature \( T_C \), and only then enters into the chiral phase at a lower temperature \( T_{Ch} \). The initial triple-\( Q \) state is entered when \( \psi_0 \) first becomes non-zero. Assuming that all temperature dependence is contained in the coefficient \( a_0 \), we thus write \( a_0 = \tilde{a}(T - T_C) + a_1 (1 - \gamma) \). Using this definition, and minimizing the Landau free energy with respect to \( \psi_0 \), the order parameter amplitude acquires the temperature dependence \( \psi_0^2 = 2\tilde{a}(T_C - T)/(15c_0 + 8d_0 + 6c_2) \). The chiral state emerges when \( 9c_2 \psi_0^4 = 2a_1 (1 - \gamma) \), so that finally we find its transition temperature to be \( T_{Ch} = T_C - a_1 (1 - \gamma)/(15c_0 + 8d_0 + 6c_2)/(9a_2) \).

From equation (2), it is straightforward to see that both the free energy itself and its first derivative with respect to temperature are continuous across \( T_{Ch} \). The second derivative however, which is proportional to the specific heat, has a jump-like discontinuity:

\[
C_V = \begin{cases} 3a_1^2 T/[15c_0 + 8d_0 + 6c_2] & T > T_{Ch} \\ 3a_1^2 T/[15c_0 + 8d_0 - 3c_2] & T < T_{Ch} \end{cases}
\tag{3}
\]

The transition is therefore found to be of second order.

3. Observing the transition

The phase transition between the non-chiral and the chiral charge ordered states predicted to occur at \( T_{Ch} \) has not been experimentally observed yet. The recent observation of the chiral phase in TiSe\(_2\) employed low-temperature scanning tunneling microscopy (STM), and found the chiral phase to be present throughout the studied temperature range [1]. The transition temperature must thus lie above 84 K, but below \( T_C = 202 \) K. Besides the extension of the STM study to higher temperatures, a variety of alternative experimental probes can be used to observe the transition between the two types of charge order.

It has already been shown that optical reflectometry for example is sensitive to the breakdown of rotational symmetry associated with the formation of chiral order [1]. The triple-\( Q \) mode either shares the symmetry of the lattice, or breaks it down to a threefold symmetry. The chiral
phase on the other hand is at most twofold symmetric. This difference can be observed in the varying intensity of reflected light with changing polarization.

Alternatively, one can study the distortions of the atomic lattice directly in diffraction experiments. The space group of the high temperature phase of TiSe$_2$ is lowered from P$\bar{3}$m1 to P$\bar{3}$c1 as the triple-$Q$ pattern sets in. The chiral phase breaks the symmetry down further, so that only a P2 space group remains. This change in symmetry is accompanied by an alteration of the reflection conditions. Whereas the triple-$Q$ state has forbidden reflections at $[h, -h, 0, 2l]$, the chiral state has no such constraints.

Finally, one can also make use of the fact that the formation of chiral charge order in TiSe$_2$ coincides with the appearance of an ordered structure in the orbital occupations. Because the different components of the displacement wave transfer charge between different sets of orbitals, and because one component dominates in each atomic layer, the orbital order is inevitable. The orbital-specific nature of resonant inelastic X-ray scattering (RIXS) experiments may be used to probe this orbital order in the chiral state.

4. Conclusions
The recently observed chirality in the layered dichalcogenide $1T$-TiSe$_2$ emerges from the simultaneous formation of orbital and charge density wave order. The three components of the charge density wave involve three distinct sets of orbitals, giving rise to three distinct polarization directions for their associated displacement waves. Superposing the components with non-zero relative phase differences then yields the observed chiral pattern. The origin of these phase differences can be understood from a Landau expansion of the free energy, in which the competition between local Coulomb interactions and elastic energy yields two possible phases for the charge order in TiSe$_2$. At the initial charge ordering temperature, the phase differences are strictly zero, and the charge density wave is non-chiral. At a second, lower temperature another phase transition is encountered and the phase differences become non-zero, yielding a chiral charge ordered state. The transition into the chiral state can be observed using a variety of experimental probes, including scanning tunneling microscopy, optical reflectometry, diffraction and inelastic X-ray scattering.

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